



X-ray Tracking of Electronic and Structural Dynamics During Chemical Reactions Using Free Electron Lasers

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X-ray Tracking of Electronic and Structural Dynamics During Chemical Reactions Using Free Electron Lasers

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PhD Thesis 2018

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Abstract

Many transition metal complexes have optical properties which can be utilized in the study of fundamental and applied photochemistry. In some cases these complexes can be used in solar cell applications and for photo-catalysis. How these complexes function in practical applications is connected to their excited state molecular structure and their excited state energy landscape. The photophysical nature of the excited state of the complex entails that the complex will inevitably relax back into the ground state, sometimes via one or more intermediate states. The energy flow associated with this relaxation process is related to the degrees of freedom and the vibrational modes of the molecule and is of significant interest in relation to the design of new compounds with tailored properties.

This thesis describes the ultrafast photochemistry of several different transition metal complexes studied using Time-Resolved Wide Angle X-ray Scattering (TR-WAXS) at X-ray Free Electron Lasers (XFEL's). First, the thesis describes the theoretical background of how X-rays can be utilized to reveal the structure of matter and the role of X-ray scattering for the study of the photochemistry of transition metal complexes in solution. The technique of TR-WAXS is outlined and the associated data reduction and treatment is described.

The first system studied, using TR-WAXS, is the ruthenium based complex, $[\text{Ru}_3(\text{CO})_{12}]$. Following photo-excitation, this complex undergoes a series of structural changes, including bond breakage and reformation. Our experiments and analysis address how this reaction process occurs on the <50 ps timescale. The experimental data is modelled using density functional theory (DFT) and molecular modelling. From our analysis several intermediate structures are suggested including a previously not reported intermediate. All intermediates suggested by our analysis, save the new intermediate, are reported by complementary optical techniques. Thus, combining the new XFEL based results with existing literature generates a suggestion for a complete and consistent picture of the photo-fragmentation cycle of $[\text{Ru}_3(\text{CO})_{12}]$.

The second system studied is a di-platinum complex, $[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]^{-4}$ (abbreviated PtPOP) coordinated to thallium (Tl-PtPOP). The ultrafast picosecond (<5 ps) dynamics of the system was studied with optical Transient Absorption and TR-WAXS. Time-domain Fourier transform of the experimental data of the two techniques show

two distinct temporal modes, which was assigned the vibrational modes of Tl-Pt and Pt-Pt. The TR-WAXS data was modelled using DFT structural optimization and previously unknown ground state structure of Tl-PtPOP was suggested. Based on this structure the ultrafast structural dynamics ($t < 5\text{ps}$) of Tl-PtPOP was interpreted from the XFEL data through a structural optimization of the excited state structure.

The final part of the thesis regards the role of the X-ray energy on a TR-WAXS structural analysis. With the access to larger X-ray energies a typical TR-WAXS experiment has access to larger scattering vectors. How this effects a TR-WAXS structural analysis was studied through the modelling of simulated TR-WAXS experimental data. Modelling the simulated data using an incomplete model shows that the prediction power of an incomplete model increases with an increase in X-ray energy.

Resumé

Mange overgangsmetalkomplekser har optiske egenskaber, som kan bruges til at studere fundamental og anvendt fotokemi. I nogle tilfælde har disse komplekser mulige anvendelser i solcelleteknologi og i fotokatalyse. Hvor godt disse komplekser fungerer i praktiske anvendelser, er forbundet til deres molekylære strukturer og deres energilandskab i den exciterede tilstand. Et kompleks i en exciteret tilstand vil over tid relaxere tilbage til grundtilstanden. Undervejs i denne proces kan komplekset danne et eller flere mellemprodukter. Helt præcist hvordan denne relaxeringsproces foregår, er forbundet til kompleksets frihedsgrader og vibrationelle tilstande, hvilket har betydelig interesse i forbindelse med design af nye molekyler med skræddersyede egenskaber.

Denne afhandling beskriver den ultrahurtige fotokemi af forskellige overgangsmetalkomplekser undersøgt med tidsopløst bred-vinkel røntgenspredning (TBVRS) på røntgen-fri-elektronlaser (RFEL) kilder. Først beskriver afhandlingen den teoretiske baggrund for, hvordan røntgen kan bruges til at undersøge strukturen af materialer, og hvilken rolle røntgenspredning har i undersøgelser af overgangsmetalkomplekser i opløsning. Desuden bliver tidsopløst bredvinkel røntgenspredning og den tilhørende databehandling beskrevet.

Det første system, som er undersøgt ved brug af TBVRS, er det ruthenium-baserede kompleks, $[\text{Ru}_3(\text{CO})_{12}]$. Når fotoexciteret vil dette kompleks gennemgå en række strukturelle ændringer inklusiv brydning af bindinger for til sidst at blive gendannet. Vores eksperimenter og tilhørende analyse adresserer, hvordan denne proces foregår på en <50 ps tidsskala. Det eksperimentelle data er analyseret ved brug af densitet-funktional-teori (DFT) og molekylær modellering. Vores analyse foreslår eksistensen af flere mellemprodukter, herunder et mellemprodukt som ikke før er observeret. Alle mellemprodukter, som vores analyse foreslår, er før observeret ved brug af andre optiske teknikker på nær det nye mellemprodukt. Ved at kombinere vores nye RFEL-baserede resultater med eksisterende litteratur har vi foreslået et komplet og konsistent billede for fotofragmenteringen af $[\text{Ru}_3(\text{CO})_{12}]$.

Det andet system undersøgt er $[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]^{-4}$ (forkortet PtPOP) koordineret til tallium. Den ultrahurtige dynamik af systemet er undersøgt med optisk transient absorption og TBVRS. Tidsdomæne Fourier transformationen af det eksperimentelle data fra de to teknikker viser to frekvenser, som er tilskrevet de vibrationelle tilstande af

Tl-Pt og Pt-Pt. TBVRS-data er analyseret ved brug af DFT-strukturel optimering, og baseret på denne analyse foreslår vi en hidtil ukendt struktur for grundtilstanden af Tl-PtPOP. Ved brug af denne struktur er den ultrahurtige strukturelle dynamik ($t < 5$ ps) af TlPtPOP fortolket fra RFEL-data igennem en strukturel optimering af strukturen i den exciterede tilstand.

Den sidste del af afhandlingen angår rollen som røntgenenergien spiller i en TBVRS-strukturel analyse. Med adgang til højere røntgenenergier vil et typisk TBVRS kunne opnå adgang til spredningsvektorer. Hvordan dette påvirker en TBVRS-strukturel analyse, er undersøgt ved at modellere simuleret TBVRS eksperimentel data. Ved at modellere den simulerede data med en ufuldstændig model vises det, at en ufuldstændig model gør gavn af adgangen til højere røntgenenergier.

Acknowledgements

As I open this tex file, I am immediately filled with fond memories from the three years of my PhD. This PhD has given me the opportunity to travel around the globe to do science on the mind blowing time scale of atoms using billion dollar machinery. An amazing experience! Along the way I have met many wonderful people whom I feel lucky to have met and I have a lot of people to thank. So lets get started!

First and foremost I would like to thank my supervisors, Martin Meedom Nielsen and Kristoffer Haldrup for hiring me and giving me the opportunity of being part of awesome science. I want to thank you for both for always being willing and eager to impart your immense knowledge, not only on matters related to science but also on other aspects of life. You have showed me nothing but kindness and I have thoroughly enjoyed working along side you both. I couldn't have asked for better people to supervise me.

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Til min mor og mine søskende. Kære mor, Janus, Søren og Lise. Tusinde tak for jeres forståelse og støtte igennem min PhD. Uden den havde jeg for længst opgivet. Jeg sætter pris på jer og elsker jer alle.

To that special someone in my life: Dear coffee. Thank you for getting me up in the morning and for keeping me awake in the long hours of beamtimes.

And last but not least. Thank you to the big flying spaghetti monster for touching me with thine noodly appendages and to God for making me an atheist.

List of publications

This chapter contains the list papers of which I am **author/coauthor**. Under the author list of each paper the *state* of each paper is shown. In the following chapter a description of my scientific contribution to each paper is given. Papers in this section will be referenced to throughout the thesis using the Roman numerals. The full length version of the papers can be found in the appendix.

I Tracking the picosecond deactivation dynamics of a photoexcited iron carbene complex by timeresolved X-ray scattering.

Denis Leshchev, Tobias C. B. Harlang, Lisa A. Fredin, Dmitry Khakhulin, Yizhu Liu, Elisa Biasin, **Mads G. Laursen**, Gemma E. Newby, Kristoffer Haldrup, Martin M. Nielsen, Kenneth Warnmark, Villy Sundstrom, Petter Persson, Kasper S. Kjær and Michael Wulff.

Published. Chemical science. DOI: 10.1039/C7SC02815F

II Anisotropy enhanced X-ray scattering from solvated transition metal complexes.

Elisa Biasin, Tim B. van Driel, Gianluca Levi, **Mads G. Laursen**, Asmus O. Dohn, Asbjørn Moltke, Peter Vester, Frederik B. K. Hansen, Kasper S. Kjær, Tobias Harlang, Robert Hartsock, Morten Christensen, Kelly J. Gaffney, Niels E. Henriksen, Klaus B. Møller, Kristoffer Haldrup and Martin M. Nielsen.

Published. Journal of synchrotron radiation. DOI: 10.1107/S1600577517016964

III Solvent Manipulation of Charge Transfer Excited State Relaxation Pathways in $[\text{Fe}(\text{2,2'}\text{-bipyridine})(\text{CN})_4]^{2-}$

Kasper S. Kjær, Kristjan Kunnus, Tobias C. B. Harlang, Tim B. Van Driel, Kathryn Ledbetter, Robert W. Hartsock, Marco E. Reinhart, Sergey Koroidov, Lin Li, **Mads G. Laursen**, Elisa Biasin, Frederik B. Hansen, Peter Vester, Morten Christensen, Kristoffer Haldrup, Martin M. Nielsen, Pavel Chabera, Yizhu Lui, Hideyuki Tatsuno, Cornelia Timm, Jens Uhlig, Villy Sundstöm, Zoltan Nemeth, Dorottya Szemes, Eva Bajnoczi, Gyorgy Vanko, Roberto Alonso Mori, James M. Glowina, Silke Nelson, Marcin Sikorski, Dimosthenis Sokaras, Henrik T. Lemke, Sophie Canton, Kenneth Wärnmark, Petter Persson, Amy A. Cordones, Kelly J. Gaffney.

Published. Physical Chemistry Chemical Physics. DOI: 10.1039/C7CP08011E

IV Initial metal-metal breakage detected by fs X-ray scattering in $\text{Ru}_3(\text{CO})_{12}$ photolysis at 400 nm

Qingyu Kong, **Mads G. Laursen**, Kristoffer Haldrup, Kasper S. Kjær, Elisa Biasin, Tim B. van Driel, Dmitry Khakhulin, Michael Wulff, Victoria Kabanova, Rodolphe Vuilleumier, Savo Bratos, Martin M. Nielsen, Kelly J. Gaffney, Tsu-Chien Weng, Michel H. J. Koch.

Submitted.

V An ultrafast molecular movie reveals that dispersion interactions control the photochemistry of diiodomethane in solution.

Matthijs R. Panman, Elisa Biasin, Oskar Berntsson, Markus Hermann, Stephan Niebling, Ashley J. Hughes, Joachim Kübel, Kalina Atkovska, Emil Gustavsson, Asmus O. Dohn, **Mads G. Laursen**, Diana B. Zederkof, Alireza Honarfar, Kensuke Tono, Tetsuo Katayama, Sigeki Owada, Tim Brandt van Driel, Kasper Kjaer, Martin M. Nielsen, Jan Davidsson, Jens Uhlig, Kristoffer Haldrup, Jochen S. Hub, Sebastian Westenhoff.

Submitted.

VI Shedding Light on the Nature of Photoinduced States Formed in a Hydrogen Generating Supramolecular RuPt Photocatalyst by Ultrafast Spectroscopy

Annemarie Huijser, Qing Pan, David van Duinen, **Mads G. Laursen**, Amal El Nahhas, Pavel Chabera, Qingyu Kong, Xiaoyi Zhang, Grigory Smolentsev, Kristoffer Haldrup, Wesley R. Browne and Jens Uhlig.

Submitted.

VII Ultrafast X-ray scattering measurements of coherent structural dynamics on the ground-state potential energy surface of the Pt_2POP_4 molecule

Kristoffer Haldrup, Gianluca Levi, Elisa Biasin, Peter Vester, **Mads G. Laursen**, Frederik Beyer, Kasper Skov Kjær, Tim Brandt van Driel, Tobias Harlang, Asmus O. Dohn, Robert Hartsock, Silke Nelson, James M. Glowina, Henrik T. Lemke, Morten Christensen, Kelly Gaffney, Niels E. Henriksen, Klaus B. Møller, and Martin M. Nielsen.

In preparation. Advanced draft.

VIII Bond formation and structural relaxation in TiPtPOP studied with ultrafast time resolved X-ray scattering.

Asbjørn Molkte, **Mads G. Laursen**, Martin Meedom Nielsen, Kristoffer Haldrup.

In preparation. Early draft. Author list subject to change.

IX Improving structural determination with high energy TR-WAXS.

Mads G. Laursen, Asbjørn Molkte, Elisa Biasin, Kristoffer Haldrup, Frederik Beyer, Kasper Skov Kjær, Tim Brandt van Driel, Tobias Harlang, Martin M. Nielsen.

In preparation. Early draft. Author list subject to change.

X Ultrafast dynamics in photoexcited iron-Carbene molecules.

Lise Ørdu Sandberg, Tobias C. B. Harlang, **Mads G. Laursen**, Elisa Biasin, Peter Vester, Martin Meedom Nielsen, Kristoffer Haldrup.

In preparation. Early draft. Author list and title subject to change.

XI Investigating the Interplay Between Electronic Configuration and Geometric Structure in Relation to Functionality of a Novel Iron Photosensitizer.

Tobias C. B. Harlang, Kasper Skov Kjær, Tim Brandt van Driel, Elisa Biasin, **Mads G. Laursen**, Lise Ørdu Sandberg, Peter Vester, Kristoffer Haldrup, Martin Meedom Nielsen.

In preparation. Early draft. Author list and title subject to change.

Contributions to publications

This chapter outlines my contributions to the publications presented in the previous chapter. For clarification: The term "online" here represents work carried out during the experiment while "offline" refers to work carried out post experiment.

I - TR-WAXS experiments. Scientific discussions.

II - TR-WAXS experiments. Scientific discussions.

III - X-ray emission spectroscopy experiments. Scientific discussions.

IV - TR-WAXS experiments. Online and Offline data reduction. Scientific discussions.

V - TR-WAXS experiments. Online data analysis. Scientific discussions.

VI - X-ray absorption spectroscopy experiments. Online data analysis. Scientific discussions.

VII - TR-WAXS experiments. Online data analysis. Scientific discussions.

VIII - TR-WAXS experiments. Offline data reduction. Data analysis. Co-writer of the paper. Scientific discussions. This paper will be a shared first authorship between Asbjørn and I.

IX - TR-WAXS simulations and analysis. Lead writer of the paper. Scientific discussions.

X - TR-WAXS experiments. Online TR-WAXS data analysis. Offline data reduction. Scientific discussions.

XI - X-ray emission spectroscopy experiments. Scientific discussions.

Introduction 1

X-rays were first systematically studied in 1895 by Wilhelm Röntgen. The term "X-rays" were coined by Röntgen to describe the (at the time) unknown type of radiation [1]. Using the Crookes glass electric discharge tube Röntgen studied the glow appearing after exposing a low pressure air environment to a high DC voltage [2]. The observed glow was the yellow/green fluorescence created as a result of the high DC voltage ionizing the air particles and accelerating electrons into the walls of the glass tube. The energy of the accelerated electrons are determined by the voltage and if set sufficiently high the bremsstrahlung process results in the creation of X-rays. Before 1895 some effects of X-rays had been observed but never fully understood. The systematic study by Röntgen opened up the door for the pioneering X-ray science in the century to come. The usage of X-rays in science are many; ranging from the study of materials to medical applications. Indeed, no introduction to X-ray science should come without showing the famous X-ray photograph of the hand of Röntgen's wife. As shown in Figure 1.1 Röntgen demonstrated the power of X-rays in medical science by X-ray imaging.



Figure 1.1: X-ray photograph of the hand of Anna Bertha Ludwig, the wife of W. Röntgen. [3]

Since their discovery, X-rays have played a central role in the characterization of materials. In the start of the 20th century the Bragg family used X-ray diffraction to study the building blocks of all materials, namely the atom.

Fast forward to the late 20th century. Here X-rays found their use in the field of femtochemistry as a means to investigate the structures associated with chemical reactions. The field of femtochemistry was founded in 1987 and pioneered by Ahmed H. Zewail [4]. The focus of femtochemistry is the study of the various intermediate steps involved chemical reactions i.e bond breakage/formation or atomic rearrangements. As a chemical reaction takes place several intermediate products may be formed in the process. While the intermediate products are no longer present in the end products, they are vital for the understanding of the mechanisms in a chemical reaction. Most chemical reactions occur on the (extremely rapid) time scale of atomic movement; the femtosecond (one quadrillionth of a second!). Thus special techniques are required in order to capture the mechanisms of a chemical reaction. In femtochemistry the intermediate products are examined by ultra short (temporally) pulses of light. An initial pulse triggers the chemical reaction while a delayed pulse serves as the investigative probe. This pump and probe method is at the heart of the X-ray tracking of structural dynamics of chemical reactions.

1.1 Transition metal complexes

The chemical reactions studied in this thesis are the photo-activated chemical reactions of transition metal complexes. A transition metal complex (TMC) is a coordination complex. In a coordination complex a central atom/ion is bound to surrounding structure of molecules/ions. The surrounding structure is called the ligand and when the central atom is of the transition metal variety, the complex is called a transition metal complex. To fully capture the elusive details of a photochemical reaction of a TMC, often requires the combination several optical and X-ray techniques [5]. However, the technique primarily used in this thesis is that of Time Resolved Wide Angle X-ray Scattering, a technique which is described in [6] and introduced in Section 2.3.

There are several properties of TMCs which makes them an ideal subject of study. TMCs have large scattering cross sections, which is important from an experimental point of view, as it enables readily detectable signals from X-ray experimental techniques. In addition, TMCs exhibit absorption bands in the visible region, which has its use in solar cell applications. In these types of TMCs, the understanding the relaxation pathway of the excited state is important, as it desired to increase the lifetime of their Metal-to-Ligand Charge Transfer (MLCT) states. In a MLCT state the electron is primarily located on the ligand structure as opposed to metal centered (MC) states where the electron is primarily located on the metal center. These states play a vital part in a TMCs ability to function as a solar cell, as long lived MLCT states are required

for the extraction of electrons. The interplay between MLCT lifetimes and the molecular structure of TMCs is treated in our recent X-ray scattering and X-ray emission spectroscopy studies of iron-centred carbenes on both picosecond [I] and femtosecond timescales [X], [XI]. The combination of these studies show that the ligand structure effects the energy level of the (unwanted) metal centred state. This makes it possible to design TMC where the MLCT state more energetically favourable increasing the MLCT life time. The energy levels and relaxation pathways can also be affected by the choice of solvent as we show for the iron-centred complex, $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ in [III]. In [VI] we utilize transient optical absorption and X-ray absorption spectroscopy to study the charge transfer states of a hydrogen generating ruthenium platinum complex. Here the charge transfer state is important for the catalytic properties of the molecule as the catalytic site becomes active in the excited charge transfer state.

In [IV] and [V] we studied bond breakage and bond formation by the photo-dissociation and recombination of the model systems, triruthenium dodecacarbonyl, $[\text{Ru}_3(\text{CO})_{12}]$, and diiodomethane, CH_2I_2 in solution. In the photo-dissociation process, intermediate structures are formed and the exact nature of how these structures are formed and how they interact with the solvent is interesting from a fundamental chemistry point of view. The intermediate structures are also important as these can have catalytic properties as is the case of $[\text{Ru}_3(\text{CO})_{12}]$. Additionally, understanding the role of the solvent is paramount as all chemistry occur in solution.

A class of TMC's useful for the study of bond dynamics is found in di-metal d^8 - d^8 systems (e.g Pd^{II} , Pt^{II} , Rh^{I} , Ir^{I} systems) [7]. Many of these systems have an partially filled anti bonding molecular orbital in the ground state and can upon photo excitation transition into a bonding orbital. One such TMC is the di-platinum model system, $[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]^{4-}$ (abbreviated, PtPOP) which we have used to study scattering anisotropy [II], coherent structural dynamics [VII] and the bond dynamics of thallium ions and PtPOP [VIII]. How the experimental technique used in these studies can be improved using high energy X-rays is the focus of [IX].

The scientific research of this thesis can overall be divided into two; the study of charge transfer states [I,III,VI,X,XI] and bond dynamics such as bond formation and photolysis [II,IV,V,VII,VIII,IX]. However, my primary effort has been on the latter and will thus be the focus of the thesis.

To fully understand how X-rays may be used to capture the elusive details of a chemical reaction some theoretical background is required and is presented in the following chapter.

X-ray scattering as a structural probe 2

The purpose of this chapter is to introduce some of the fundamental concepts that can occur when X-ray photons interact with matter. When an X-ray photon is within proximity of matter, three things can happen; the X-ray photon is absorbed, scattered or it passes unhindered through the matter. The processes related to absorption and scattering are many and books have been dedicated to the full description of these. Here I restrict myself to the introduction of the overarching terms of the X-ray interactions relevant for this thesis. Namely selected subjects within the topic of X-ray scattering and the sources used to create X-rays.

2.1 Synchrotrons and X-ray Free Electron Lasers

Electrons when accelerated sufficiently will emit X-rays. Several machine designs of how to utilize this to efficiently produce usable X-rays exist. Most practical applications of X-rays require a bright source. In addition, several fields of study require a pulsed source. The necessity of a pulsed source has root in the desire to understand ultrafast phenomena. X-ray detectors do not have the "shutter speed" needed to capture the ultrafast physics of atomic motion. The workaround is to utilize temporally short pulses to probe a system and thus capture a series of snapshots much like a motion picture. This section will focus on the description of two types of pulsed X-rays sources: The synchrotron and the X-ray Free Electron Laser (XFEL).

The Synchrotron

The principle design of a synchrotron is shown in the left hand side of Figure 2.1. In a synchrotron the first point of operation is at the electron gun. The electron gun emits electrons (in bunches) which are then collected and accelerated by a linear accelerator (LINAC). After the acceleration by the LINAC the electrons enter a booster ring which further accelerates the electrons. Finally, the electrons enter the storage ring. The storage ring consists of many straight line segments connected to each other at an angle forming a shape with the resemblance of a ring (thus storage ring). At each intersection

of the line segment there is a bending magnet which serves to direct the electrons from one line segment into the next and in the process produce X-rays. In addition to the bending magnets, each line segment may have an insertion device, such as, a wiggler or an undulator. These insertion devices use periodically alternating north and south pole permanent magnets to move electrons back and forth in a sinusoidal pattern [10]. At each turn of the sinusoidal pattern X-rays are emitted and at the end of the line segment these are directed into an experimental station (a beamline). The beamlines house the optics and experimental equipment needed to utilize the X-rays for scientific investigations. The temporal width of the X-ray pulses are on the order of 100 ps and are limited by the temporal width of the electron bunches. [9]

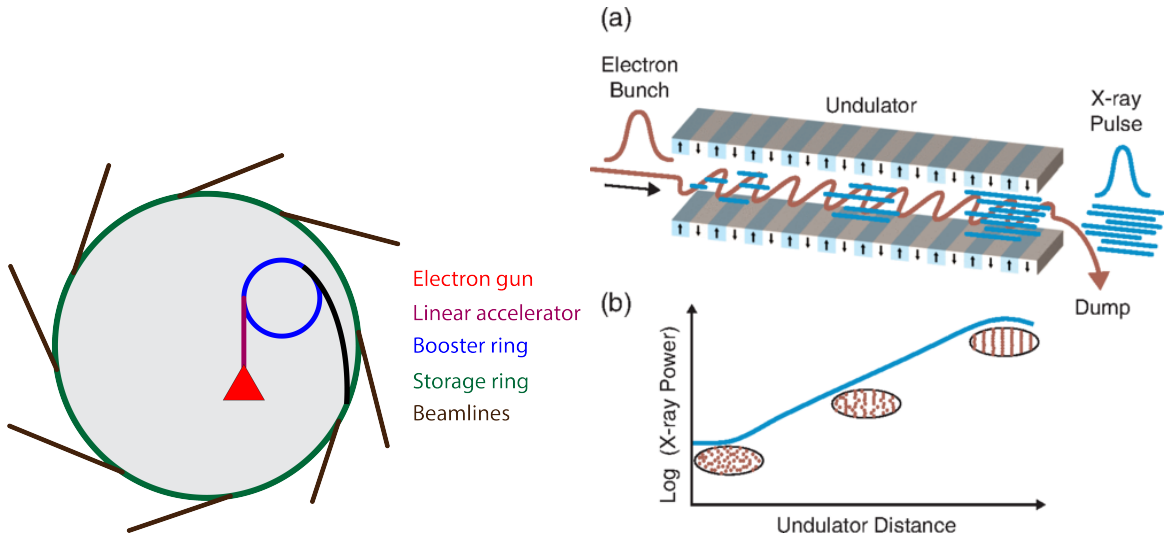


Figure 2.1: Left: Conceptual design of a synchrotron showing the key elements: The electron gun, the LINAC, the booster ring, the storage ring and the beamlines. Right: Overview of the SASE process enabled by a long undulator. Figure from [11]

The X-ray Free Electron Laser

In part due to the temporal limitations of the synchrotron radiation the X-ray Free Electron Laser (XFEL) was developed. The XFEL enables the production of X-ray pulses with temporal width in the femtosecond regime. As opposed to the synchrotron the XFEL does not have a ring in which the electrons travel. Instead, electrons (bunches at a time) are accelerated directly into a long undulator (much longer than the insertion devices found at synchrotrons). When the undulator is sufficiently long the travelling electron bunches undergo the process of Self Amplified Spontaneous Emission (SASE). The SASE process occurs as the X-rays emitted from a given electron bunch interact resonantly with the electron bunch [11]. The resonant interaction gives rise to micro-bunching where the electrons within a bunch form a spatially periodic electron distribution as illustrated in Figure 2.1, right hand side. This has the effect of producing temporally short femtosecond X-ray pulses with much higher peak brilliance (increased by a factor of 10^9) than that of the synchrotron X-ray pulses. Additionally

the X-ray pulses have a high degree of transverse coherence. However, the spontaneous nature of the SASE process has the disadvantage of fluctuations in the X-ray energy and intensity of the pulses. Also, as opposed to the synchrotron a fewer number of beamlines can be operated at a given time at an XFEL.

2.2 X-ray scattering

Subjects related to X-rays and electromagnetic waves in general have been covered extensively in textbooks such as [12]. Electromagnetic waves are typically subdivided into regions of certain energy ranges and are given names for clarity. Examples of low to high energy ranges are the radio waves, visible light and X-rays. Common for all electromagnetic waves is that they are characterized by their wavelength, λ or wavevector $|\mathbf{k}| = 2\pi/\lambda$. In the mathematical description of a propagating electromagnetic wave the wavevector has the direction in which the wave propagates. The electric field part of the wave may be expressed as

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0 e^{i(\mathbf{k}\mathbf{r} - \omega t)}, \quad (2.1)$$

where $\mathbf{r}$ is the spatial position, ω is the frequency of the wave and t is time. The magnetic part of the wave has a similar expression as

$$\mathbf{B} = \frac{1}{\epsilon_0 \mu_0} \mathbf{k} \times \mathbf{E}, \quad (2.2)$$

where ϵ_0 and μ_0 are the permittivity and permeability of free space, respectively.

When an X-ray photon is scattered a change of the momentum of the photon occurs. The change in momentum is referred to as the scattering vector and is expressed through the photons initial and final wavevectors $\mathbf{k}$ and $\mathbf{k}'$ as

$$\mathbf{Q} = \mathbf{k} - \mathbf{k}'. \quad (2.3)$$

The scattering vector will be used numerous times throughout this thesis. The use of it not only simplifies mathematical expressions but also provides useful information for scattering data as the scattering vector is both connected to scattering angle, 2θ through

$$Q = \frac{4\pi}{\lambda} \sin\left(\frac{2\theta}{2}\right) \quad (2.4)$$

and the phase difference, $\Delta\phi(\mathbf{r})$, between scatters

$$\Delta\phi(\mathbf{r}) = \mathbf{Q} \cdot \mathbf{r}. \quad (2.5)$$

$\mathbf{Q}$ is connected to either a change of the direction of propagation, a change in the energy of the photon or both. If the X-ray photon only changes the direction of propagation it is referred to as elastic (Thomson) scattering while if the scattering occurs with a change in the energy of the photon it is referred to as inelastic (Compton) scattering. Elastic scattering is an important process as the interference of elastically scattered waves contain structural information of the scatterers. This is typically exemplified in textbooks by considering the simplest case, namely the scattering intensity of two electrons. In this simple case the scattering intensity is given as the modulus of the scattering amplitude with the scattering amplitude being the sum of the two scattered waves. Most atoms are many electron bodies and as in the previous case of two electrons the scattering of an atom is the sum of scattered waves from all of its electrons. Considering the electrons of the atom as being a smooth charge distribution $\rho(\mathbf{r})$ the scattering length of the atom is expressed as

$$-r_0 f^0(\mathbf{Q}) = -r_0 \int \rho(\mathbf{r}) e^{i\mathbf{Q} \cdot \mathbf{r}} d\mathbf{r}, \quad (2.6)$$

with r_0 being the Thomson scattering length of the electron and $f^0(\mathbf{Q})$ is designated as atomic form factor [13].

Most scientific cases where X-ray scattering is used, the examined system contains many atoms. In this case the scattering of N atoms may be calculated from the sum of atomic form factors, f of each atom and their respective positions $\mathbf{r}$ as

$$S(\mathbf{Q}) = r_0^2 \sum_{i,j}^N f_i^*(\mathbf{Q}) f_j(\mathbf{Q}) e^{i\mathbf{Q} \cdot \mathbf{r}_{ij}} \quad [14]. \quad (2.7)$$

This equation assumes that total scattering can be modelled as the sum of the scattering of the electron densities of the individual atoms (referred to as the Independent Atom Model (IAM)). Despite this model ignoring chemical bonding, it generally provides accurate results [15]. If the system is crystalline the atoms are ordered with repeating units. In this case the scattering interference is strong for certain scattering angles and in turn gives rise to intense scattering peaks known as Bragg peaks. For disordered systems such as molecules in dilute solutions the intensity is the sum of the scattering of molecules with all possible orientations. This averages out the phase information and as a result the scattering intensity is smeared out and is typically smoothly varying. However, it still contains structural information of the sample in question though it is the information of the orientationally averaged structure. The scattering intensity of a orientationally averaged molecular structure is

given as,

$$\begin{aligned} \left\langle \left| \sum_{j=1}^N f_j e^{i\mathbf{Q}\cdot\mathbf{r}_j} \right|^2 \right\rangle &= |f_1|^2 + |f_2|^2 + \dots + |f_N|^2 \\ &+ 2f_1f_2 \frac{\sin(Qr_{12})}{Qr_{12}} + 2f_1f_3 \frac{\sin(Qr_{13})}{Qr_{13}} + \dots + 2f_1f_N \frac{\sin(Qr_{1N})}{Qr_{1N}} \\ &+ 2f_2f_3 \frac{\sin(Qr_{23})}{Qr_{23}} + \dots + 2f_2f_N \frac{\sin(Qr_{2N})}{Qr_{2N}} + \\ &\dots + 2f_{N-1}f_N \frac{\sin(Qr_{N-1,N})}{Qr_{N-1,N}} \quad [14]. \end{aligned} \quad (2.8)$$

Equation 2.8 plays a central role when wishing to uncover the molecular structure hidden in experimental data. This is because the structure is not given directly from the experimental data but rather relies on model fitting of experimental data. The exact role of Equation 2.8 in the structural determination of molecules is further discussed in section 2.5.

TR-WAXS is an experimental technique, which uses X-ray scattering, to track how the molecular structures in photochemical reaction, evolve in time

Having introduced key elements of X-ray scattering, the foundation is set for understanding how X-ray scattering can be utilized to uncover the structure of molecules. Several experimental techniques using the principles of X-ray scattering exist. However, if one is interested in uncovering the molecular structures in a photochemical reaction (as it takes place *in situ*), the experimental technique of choice, is that of Time Resolved Wide Angle X-ray scattering (TR-WAXS).

The subsequent sections will introduce how a TR-WAXS experiment is performed and how interpret experimental data. TR-WAXS is also known under the names *time-resolved X-ray liquidography* and *time-resolved X-ray solution scattering* and is extensively covered in the review by Ihée et al. [6]. However, in this thesis the technique will be referred to as TR-WAXS.

2.3 The principles of a TR-WAXS experiment

A TR-WAXS experiment is based on the principles of laser-pump X-ray-probe, which is simple in description and hard in execution. In a laser-pump X-ray-probe experiment the photochemical response of a system of interest, e.g a transition metal complex in solution, is initiated by an optical laser pulse. After a given time delay the system is probed by an X-ray pulse and the scattering that follows is collected by a detector. As discussed in the previous chapter the X-ray scattering contains information on the molecular structure of the entire system. Thus by adjusting the temporal delay between the optical laser pulse and the X-ray probe pulse the photo-induced dynamics

can be studied on a femtosecond timescale. An illustration of a laser-pump X-ray-probe experimental setup is shown in Figure 2.2.

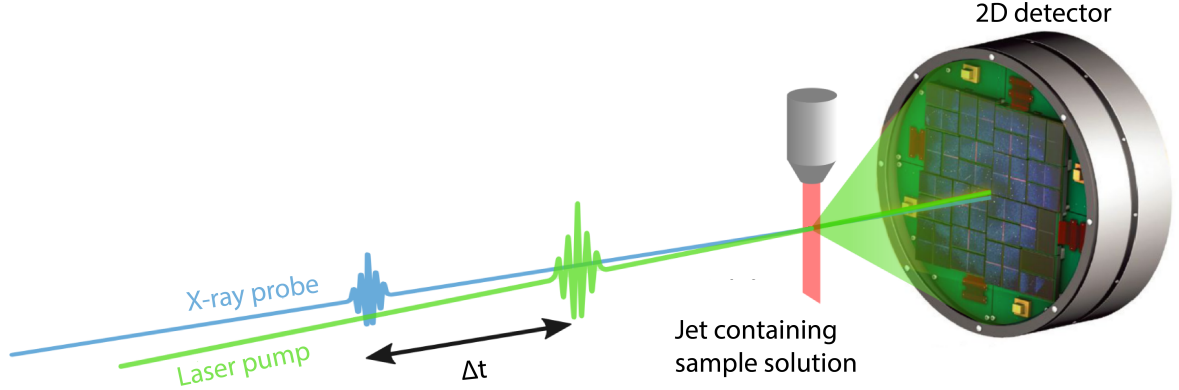


Figure 2.2: Illustration of a laser-pump X-ray-probe experimental setup. A liquid jet containing the sample solution is pumped by an optical laser pulse. After a Δt time delay the sample is probed by an X-ray pulse and the scattered X-rays are collected by the 2D detector. [16]

In the typical TR-WAXS experimental setup the sample is set to continuously flow through a capillary nozzle (with a diameter size typically ranging from 30-500 μm) after which the sample is collected and recycled. This procedure produces a free flowing circular liquid jet with flow direction perpendicular to both the laser-pump and X-ray probe pulses. The flow speed is set appropriately in order to produce laminar flow while ensuring that each laser-pump/X-ray-probe event sees fresh sample. The optical laser system varies from facility to facility. Most of the experiments related to this thesis were conducted at the XPP station [17] of the Linac Coherent Light Source [18]. Here the optical laser system is able to provide laser wavelengths of 266-800 nm with pulse durations between 10-150 fs [19] which is the relevant wavelength range and pulse duration for the time-resolved study of many photo-active transition metal complexes. The size and position of the optical laser spot is controlled using a beryllium lens and is focused onto the liquid jet. The X-ray probe is set to spatially and temporally overlap with the laser pulses on the liquid jet. In a TR-WAXS experiment both the scattering pattern of the systems ground state (no laser pump), $S(Q)_{\text{off}}$ and excited state (laser pumped), $S(Q)_{\text{on}}$, are recorded. This allows for the construction of the (1-dimensional Q -dependent) difference scattering, $\Delta S(Q)$. Exactly how the scattering collected by a 2D detector transform into $\Delta S(Q)$ is the subject of Chapter 3. The $\Delta S(Q,t)$ contain information on the structural changes between the ground state and excited state of the system as a function of time. It is a more practical quantity than $S(Q)$ as contributions such as the incoherent scattering are removed. This simplifies the process of extracting the structural dynamics of the photo-excited the TMC (from modelling of experimental data).

2.4 The structural dynamics of a photo excited transition metal complex

Once the photo chemical response of a system is initiated, intricate structural dynamics may follow as the system relaxes back to the ground state. In a photo-excited system the associated structural dynamics can be subdivided into; the dynamics of the solute, the solvent dynamics and the interplay between the solvent and solute. The latter is referred to as either the solute-solvent cross term, the solvent cage or simply the cage.

2.4.1 Solute dynamics

The solute dynamics refers to the intra-molecular structural changes the solute molecule undergoes in its photochemical cycle. Depending on the system in question the solute dynamics may entail bond breakage/formation, coherent vibrations and structural reconfigurations associated with the intermediate electronic excited states. The difference scattering of a solute,

$$\Delta S_{solute} = S_{ES} - S_{GS}, \quad (2.9)$$

is typically calculated from 2.8 using solute structures calculated from density functional theory. As evident from Equation 2.8 the scattering scales with the squared number of electrons. Thus structural change(s) of the transition metal atom(s) within the TMC dominate the structural signal of the solute.

2.4.2 Solvent dynamics

A solute molecule in its excited state will inevitably return to the ground state. In this process energy is transferred from the solute to the surrounding solvent and gives rise to change in both temperature and density of the solvent. The changes in solvent temperature and density occur on different time scales. This was shown for the photodissociation reaction of $C_2H_4I_2$ in methanol by Cammarata et al [20]. As shown in Figure 2.3 the temperature of the solvent changes after only a few picoseconds while the density change sets in on the μs time scale, as it takes time for the solvent atoms to reconfigure into a new optimum structural geometry.

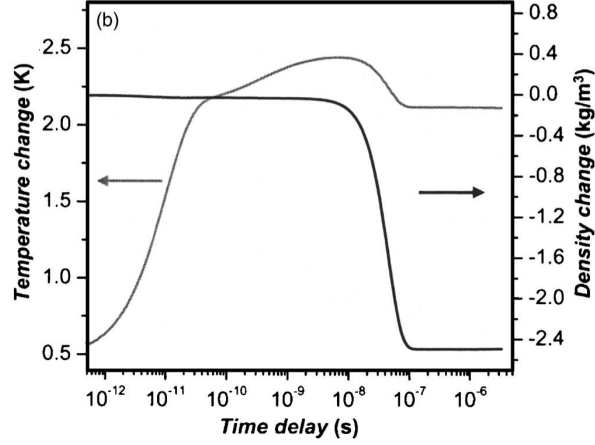


Figure 2.3: The changes in solvent temperature and density in the photodissociation reaction of $\text{C}_2\text{H}_4\text{I}_2$. The changes in the temperature occur within picoseconds while the changes in density sets in on the μs time scale. Figure from [20].

2.4.3 The solute-solvent cage

The solute-solvent cross term represents the interplay between nearest solvent shell and the solute. In a classical picture the solvent molecules in proximity of the solute experience forces related to charge distribution of the solute molecule. The charge related force primarily affect the nearest solvent molecules. Upon photo-excitation of the solute the electronic configuration change. A potential outcome is that the nearest solvent molecule react to the changed electron density of the solute by reorganising around the solute. Calculating the solute-solvent interaction can be accomplished from classical molecular modelling using the DFT structures of the solute or from more advanced quantum mechanical molecular modelling.

2.5 Analysis of TR-WAXS data

This section describes the framework in which TR-WAXS experimental data is analysed. Here data analysis should be understood as the construction of a model able to describe data. Multiple frameworks for evaluating the validity of a model exist. However, this thesis uses the χ^2 framework to compare models to data. In the χ^2 framework the validity of a model is expressed through its χ^2 value given as

$$\chi^2 = \sum_Q \frac{[\Delta S_{\text{Model}}(Q) - \Delta S_{\text{Data}}(Q)]^2}{\sigma_Q^2} / (N - M - 1) \quad [21, 22], \quad (2.10)$$

where $\Delta S_{\text{Model}}(Q)$ is the difference scattering from the structural model, $\Delta S_{\text{Data}}(Q)$ is the experimental data, N is the number of data points, M is the number of free parameters of the model and σ is the data related noise. As described previously in this chapter multiple structural changes can occur in the solute and solvent. In light of

this the structural model is commonly subdivided into the structural difference signal contributions arising from the solute, the solvent and the solvent-solute cage i.e

$$\Delta S(Q)_{Model} = \Delta S_{Solute} + \Delta S_{Solvent} + \Delta S_{Cage} \text{ [6]}. \quad (2.11)$$

As mentioned in Section 2.4.1, the solute term is typically calculated from 2.8 using solute structures calculated from density functional theory. The solvent term is often modelled using a reference measurement. In such a reference measurement the scattering signature related to solvent heating is isolated by using the heat release of an azo dye (with no ΔS solute signature) [23]. The cage term can be calculated from classical molecular modelling using the DFT structures of the solute or from more advanced quantum mechanical molecular modelling as mentioned in Section 2.4.3.

This chapter introduced the fundamental theory of X-ray scattering and how it may be used to in TR-WAXS to study photochemical reactions. The structural dynamics which may occur in a photochemical reaction was outlined and a framework for interpreting experimental TR-WAXS data was introduced. The next chapter will introduce the (non-trivial) process of treating experimental TR-WAXS data paramount for any TR-WAXS study.

Treatment of TR-WAXS data 3

A significant portion of my time as a PhD student has been spent on conducting experiments and, in extension, on the treatment and reduction of the associated data. This warrants a description of the most important aspects of the data processing. This chapter describes important elements related to the data treatment process of experimental TR-WAXS data. The purpose of describing these elements is to illuminate the (non trivial) process of going from raw experimental data to the final state of data. The latter of which is a central part of any TR-WAXS study. The data reduction and treatment elements described in this chapter have been utilized to treat and reduce the data of [IV, VIII, X].

Once the TR-WAXS data is recorded it has to undergo several processes of treatment before it is in a condition that may be analysed. The majority of the experimental TR-WAXS data related to the work in this thesis was recorded at Linac Coherent Light Source (LCLS) [18]. As such the data treatment described in this chapter is in light of the data output of the CSPAD detector [24] used at the XPP beamline [17] of the LCLS facility.

The data treatment process is in constant development. This is in part due to the development of new data treatment schemes and part due to the development of new X-ray facilities and detectors. Historically when a new detector is developed and used, a significant amount of work has to be put into understanding the detector response in order to remove systematic errors from data. This has been especially true for the first version of the CSPAD developed at LCLS. For the CSPAD detector a characterisation scheme had to be developed, in order to correct for detector related artefacts [25–27].

The data treatment scheme used in this work may roughly be categorized into two parts. The first part is to apply the necessary experimental and detector related corrections to the experimentally raw 2D scattering patterns and subsequently reduce the sheer amount of data by radially averaging the 2D detector images. This part is commonly referred to as "Data Reduction". The second part is to treat the radially averaged data (i.e the reduced data). This involves using beam diagnostics to identify

data which deviates from the average data ensemble and remove it. The removal of data based on diagnostics is referred to as "Outlier rejection". After the outlier rejection the data is scaled for the purpose of going from detector units to units from which a physical interpretation may be derived. Following this the 1D scattering signals are corrected for intensity and X-ray energy variations after which the difference signals are constructed and sorted into time bins. Each step is described in the subsequent sections.

3.1 Data Reduction

This section presents the necessary work on the raw experimental 2D scattering patterns. First a dark image of the detector is subtracted from the raw experimental 2D scattering patterns. Following this the patterns are masked and detector related corrections are applied. The now corrected patterns are then subjected to radial integration (into azimuthal bins) which reduces the sheer amount of data. Each of these steps are described remainder of this section.

3.1.1 Dark subtraction

Even when the detector is not being irradiated a current will nevertheless run through the detector and is referred to as a dark current. The dark current will contribute to the readout signal of the detector and may vary from pixel to pixel. The image created by the dark current is called the dark image and has to be subtracted from the experimentally recorded scattering patterns. Several dark images are recorded throughout the experiment and for every 20000 scattering patterns a total of 50 Dark images are averaged and used in the dark subtraction of all scattering patterns. Figure 3.1 shows the average of 50 dark images recorded in early 2015 for the experiment entitled LF78.

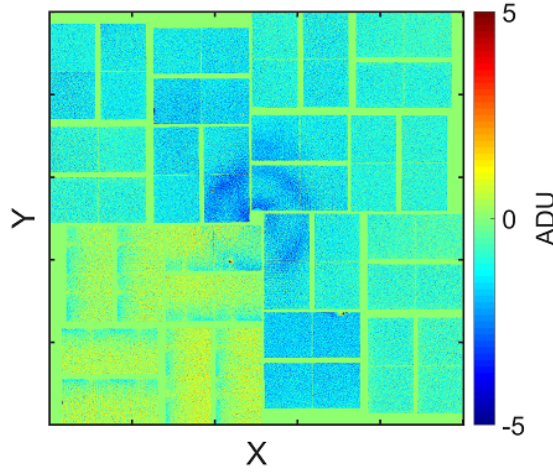


Figure 3.1: The average of 50 CSPAD dark images. Recorded in early 2015.

As can be seen from the image the dark image have visible ring shapes near the centre of the detector. This region corresponds to the region in which the liquid peak is recorded and is likely the result of the radiation damage of the detector.

3.1.2 Masking

Masking is the process of discarding pixels on the detector based on visual inspection and pixel diagnostics. The visual inspection serves the purpose of removing pixels based on experimental conditions. This typically involves the removal of pixels which are shadowed due to the experimental setup. In a less common case pixels are removed if they contain scattering from bragg peaks. This can be necessary for experiments where crystallites are formed on the nozzle throughout the experiment. Removal of pixels based on pixel diagnostics occurs through a characterization of the dark behaviour of each pixels. Pixels which have a dark readout with a high variance are discarded. In addition, the pixels at the edges of the CSPAD tiles are discarded as are the diagonal pixels as these are not active due (as per design). Figure 3.2 shows the pre and post masking used for the reduction of [VIII].

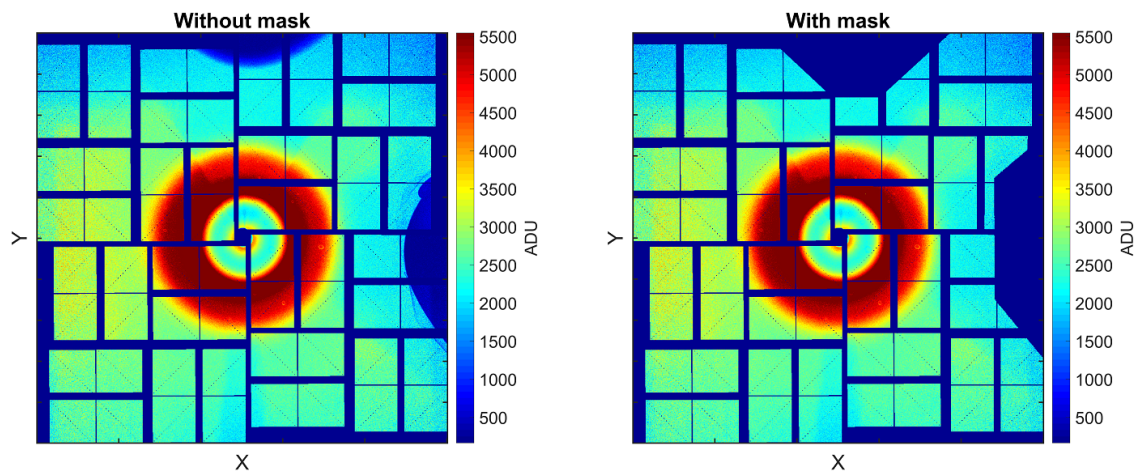


Figure 3.2: A 2D scattering patterns recorded of Tl-PtPOP in aqueous solution. Left: Without applying a mask. Right: After applying a mask.

3.1.3 Detector corrections

Several corrections have to be made to the raw 2D experimental scattering patterns as part of the reduction process. The patterns are corrected for the geometric effect of the solid angle, for the X-ray polarisation of the X-ray pulses and for the detector absorption layer efficiency. Figure 3.3 shows a scattering pattern before and after applying these correction.

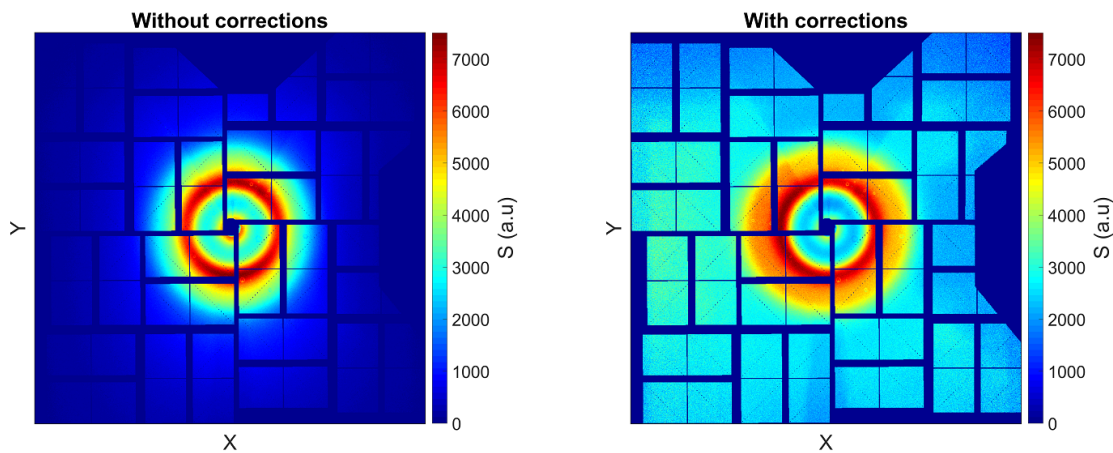


Figure 3.3: A 2D scattering patterns recorded of Tl-PtPOP in aqueous solution. Left: Before applying the corrections. Right: After applying the corrections.

The origin and need for these detector corrections are described below.

Solid Angle

The 2D scattering image has to be corrected for each pixel covering a different solid angle. The solid angle is a geometric effect which becomes significantly more important for larger scattering angles. This is because the scattering per unit solid angle has a projection area on the detector that increases with increasing scattering angles. That the scattering is spread out for larger scattering angles results in the corresponding pixels recording too few photons and thus have to be amplified. For a detector geometry set in the xy-plane as shown in Figure 3.4 the solid angle correction is given as

$$Cor_{\Delta\Omega} = \frac{p_1 \cdot p_2}{x^2 + y^2 + L_0^2} \cdot \frac{L_0}{\sqrt{x^2 + y^2 + L_0^2}} \quad [28] \quad (3.1)$$

where p_1 and p_2 are the pixel dimensions, x and y are the pixel center coordinates and L_0 is the sample-detector distance. Figure 3.5 shows the relative solid angle correction calculated for CSPAD.

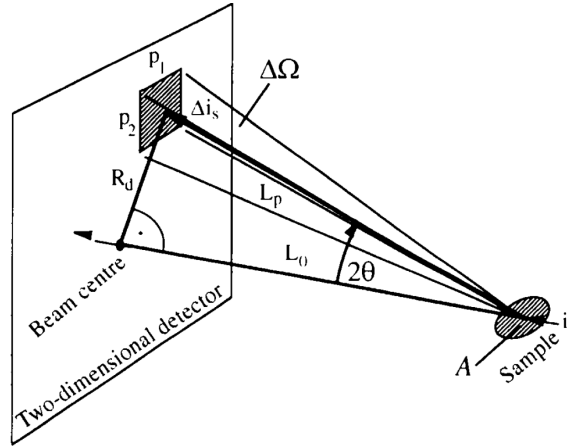


Figure 3.4: Two dimensional XY plane detector geometry. From [28].

X-ray polarisation

The large undulator of the LCLS produces X-ray pulses with a nearly linear polarisation (off by only a few percent). This in turn results in the scattered field irradiated from a given scatter having a magnitude that depends on the scattering direction. The reason for this is that the projection of the electric field vector acting on a scatterer depends on the observation point. For an observation point in the plane normal to the polarisation the full scattering is observed while an observation point in the plane of the polarisation will have a cosine dependence of the observed scattering. The X-ray polarisation correction term is given as

$$C_{Xpol} = 1 / [P(1 - (\sin \phi \cdot \sin \theta)^2) + (1 - P) * (1 - (\cos \phi \cdot \sin \theta)^2)] \quad [29] \quad (3.2)$$

where P is the polarisation, ϕ is the azimuthal angle and θ is the scattering angle. The middle of Figure 3.5 shows the polarisation correction calculated for the CSPAD.

Detector absorption layer

The active absorption layer of each pixel is a 200 micron silicon layer. As an X-ray photon propagates through the absorber layer it has a probability of being absorbed and thus detected. For larger scattering angles the X-ray path length is larger and as such the probability of absorbing an X-ray photon increases. This gives an angle dependant increase of the signal which has to be taken into account. The relative correction of the absorption between the direct X-ray beam and X-rays at a scattering angle of 2θ , C_{DAL} , is calculated as

$$C_{DAL} = \frac{1 - \exp(-\mu \cdot D)}{1 - \exp(-\mu \cdot D / \cos(2\theta))} \quad (3.3)$$

where μ is the absorption coefficient, D is the thickness of the detector absorption layer and 2θ is the scattering angle. The right hand side of Figure 3.5 shows the detector efficiency correction calculated for the CSPAD.

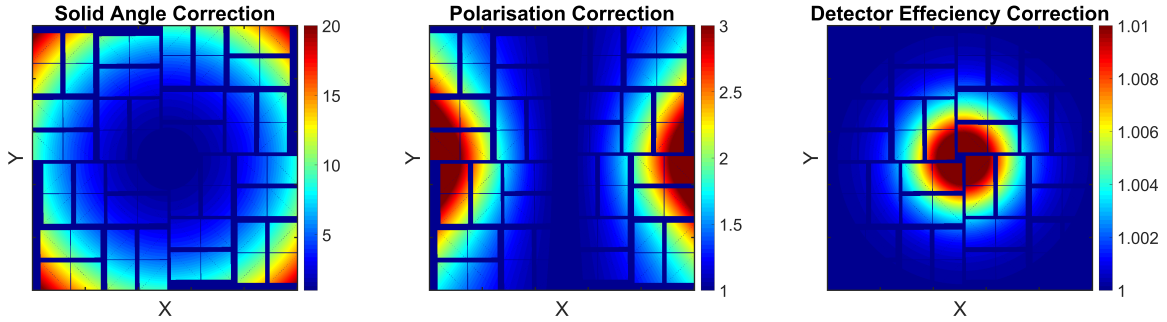


Figure 3.5: Overview of the detector related corrections. The colorbar displays the relative correction magnitude. Left: Solid Angle. Middle: X-ray polarisation. Right: Detector efficiency.

3.1.4 Determining the beamcenter and radial integration

The spatial coordinates of the X-ray beam in relation to the detector is referred to as the beamcenter. The 2D scattering patterns are centrosymmetric around the beamcenter which is key in the reduction of the data size of the raw data. Due to the centrosymmetry the 2D scattering patterns may be radially integrated virtually without loss of information. The beamcenter may be determined by subdividing a static scattering image into a set of azimuthal bins as exemplified in Figure 3.6 for 15 bins.

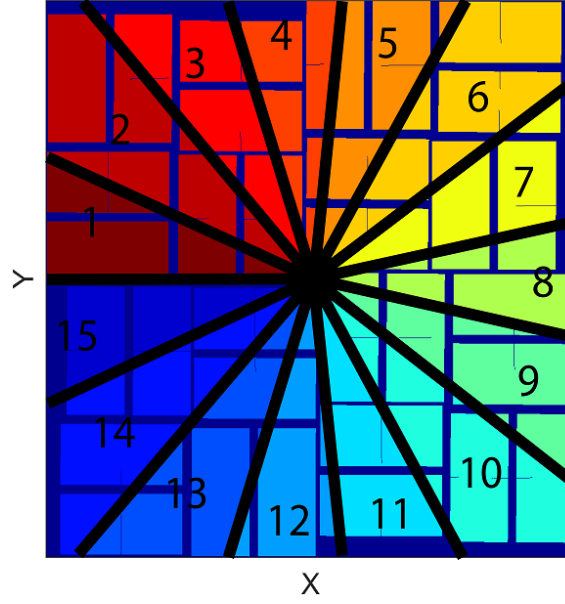


Figure 3.6: The division of the CSPAD into 15 azimuthal bins.

Each of the azimuthal bins are radially integrated to give 1d scattering curves. If the beamcenter is set correctly the scattering curve of each azimuthal bin will overlay due to radial symmetry of the static detector image. If the beamcenter is set incorrectly the radially integrated scattering curve will be smeared. Figure 3.7 shows the scattering curves obtained when radially integrating the (corrected) scattering pattern shown in Figure 3.3 using an incorrect beamcenter. The middle of the same figure shows the radial integration using a proper beamcenter. The right hand side of the figure shows the comparison of radially averaging the scattering pattern into a single bin, using a correct and incorrect beamcenter.

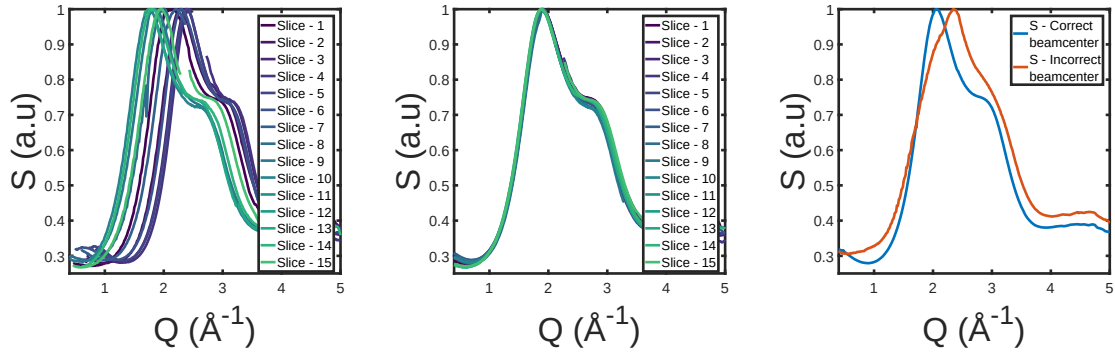


Figure 3.7: The comparison of the radially integrated scattering curves using a correct and an incorrect beamcenter. Left: The scattering curves obtained when azimuthally averaging a scattering pattern into 15 bins, using a beamcenter offset by 1 mm. Middle: The scattering curves obtained when azimuthally averaging a scattering pattern into 15 bins, using a correct beamcenter. Right: The comparison of radially averaging the scattering pattern into a single bin, using a correct and incorrect beamcenter

Radially integrating into a set of azimuthal bins also serves the purpose of separating the scattering pattern into an isotropic and an anisotropic part as discussed in section 3.3 on page 25

3.1.5 Sample-Detector distance

Correctly determining the sample-detector distance is important as it in turn determines the scattering angles for each pixel of the detector. Thus, the sample-detector distance affects both the radial integration procedure (through the binning of pixels into Q) and the scattering angle dependant corrections (Equations 3.1, 3.2 and 3.3). During an experiment the sample-detector distance is typically only known within few millimetres as the experimental setup can vary from experiment to experiment. A more precise sample-detector distance is found by comparing the experimental scattering signal with reference measurement where the sample-detector distance was measured with greater accuracy. Small corrections to the Q -axis can be made after the radial Q -binning by calculating the Q -axis for a change of sample-detector distance. This correction can be calculated as

$$\frac{Q_{d_1, 2\theta_1}}{Q_{d_2, 2\theta_2}} = \frac{\sin(\theta_1)}{\sin\left(\frac{1}{2} \tan^{-1}\left(\frac{1}{1+\Delta d/d_1} \tan(2\theta_1)\right)\right)} \quad [30] \quad (3.4)$$

where d is the sample-detector distance, Δd is the change in sample-detector distance, 2θ is the scattering angle and the subscript 1,2 designates two different sample-detector distances.

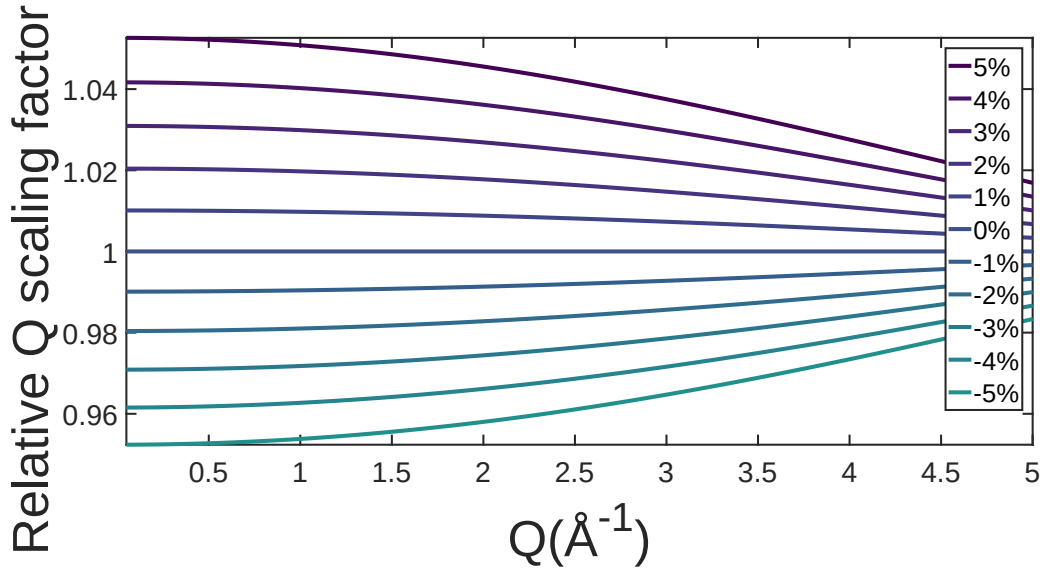


Figure 3.8: The relative Q axis correction. Shown for variations of the dectector-sample distance in the range of $\pm 5\%$

3.2 Outlier rejection

The outlier rejection described in this section refers to the discarding of data based on experimental diagnostics and statistical tools. During a scattering experiment there are several experimental conditions that vary the quality of the recorded data. The SASE process of the XFEL gives fluctuations in X-ray pulse energy, intensity and time of arrival. The liquid jet of the experimental setup can spatially drift, the flow may change from laminar to turbulent flow sporadically and/or nano crystallites can form in the sample and as a result clog the jet-nozzle either entirely or momentarily. In favourable cases a TR-WAXS experimental setup has diagnostic tools for the monitoring of the X-ray pulse energy, intensity and time of arrival. This information can form a basis for which data is rejected based on identifying X-ray shots with a behaviour outside the norm. Figure 3.9 shows a histogram of the X-ray intensity of ~ 30000 shots measured by an intensity position monitor (IPM) located upstream in the TR-WAXS experimental setup at XPP.

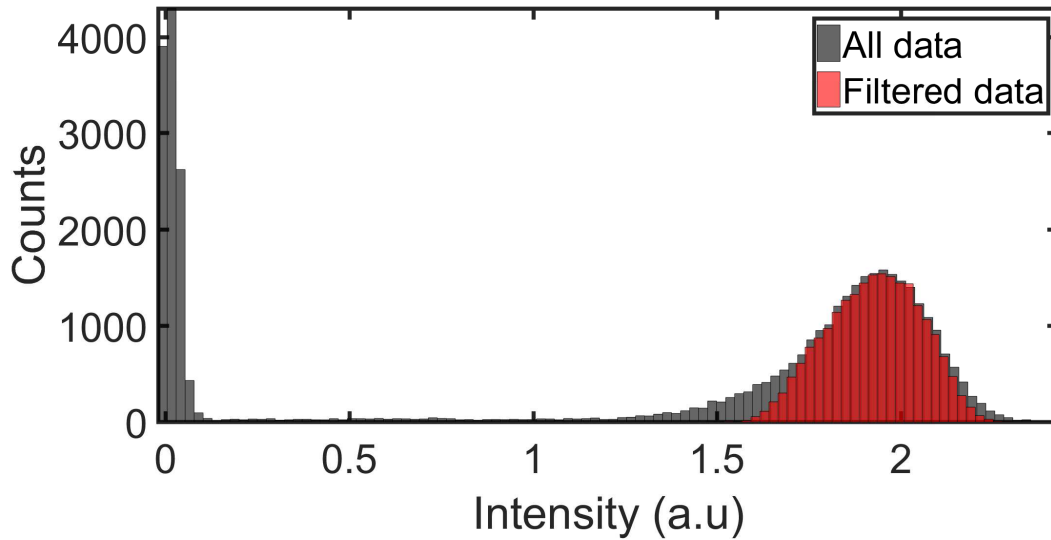


Figure 3.9: Histogram of measured intensities by an IPM. The data in black is all data while the red represents the remaining data after the data being subject to outlier rejection based on beam diagnostics.

As can be seen from figure the IPM measures a broad range of X-ray intensities. Low intensity shots are discarded as these contain a low signal-to-noise ratio. A general trend seen through the data reduction of several experiments is that outliers in data are commonly connected to X-ray shots having intensities or energies far outside the normal. Therefore it is common to discard all X-ray shots with pulse characteristics outside the norm.

3.2.1 Liquid jet behaviour

The stability of the liquid jet in a TR-WAXS experimental setup effects the data quality. Discarding data based on the behaviour of the jet is also based on the approach of identifying data outside of the norm. The behaviour of the jet may be characterized by examining the correlation between the up stream (pre-jet) X-ray intensity diode monitor and the summed counts of the detector. If the response of the diode and the detector are both linear in X-ray intensity, then the relation between the two should be linear as well, when the liquid jet operates on stable conditions. An approach to discarding shots based on the jet is to define a linear region as shown in Figure 3.10

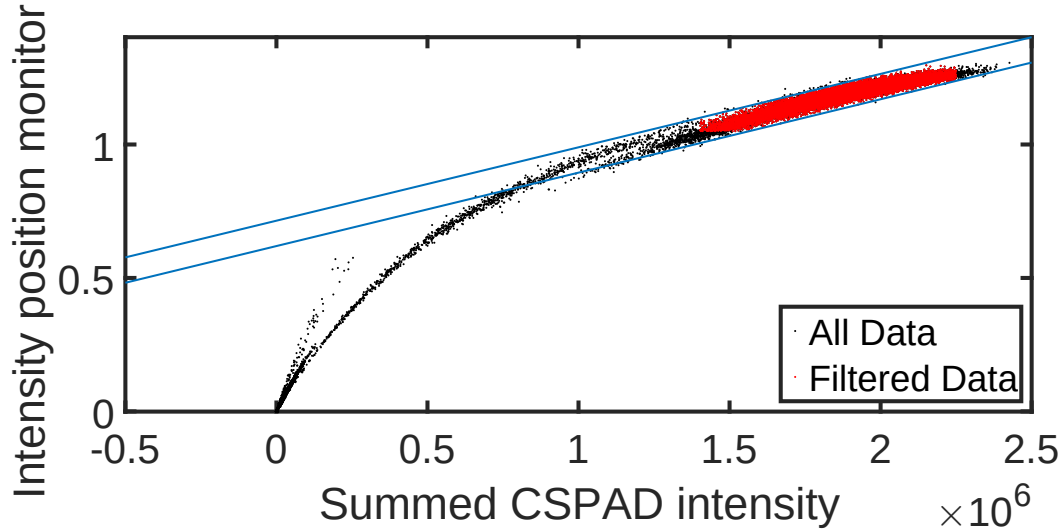


Figure 3.10: The X-ray intensity as measured by an IPM vs the summed CSPAD intensity. A linear relationship implies the liquid jet operating under stable conditions. A linear region is defined by the blue lines and data outside is rejected. The data in black is all data while the red represents the remaining data after the data being subject to outlier rejection based on beam diagnostics.

Shots outside the region defined by the blue lines are discarded.

3.2.2 Scaling to liquid unit cell

After the initial outlier rejection, based on the above considerations, the 1D scattering curves are scaled to the theoretical scattering of a liquid unit cell. Scaling the data to the liquid unit cell enables physical interpretation of the model component scalars such as excitation fraction, change in temperature and density of the bulk solvent. The theoretical scattering is calculated as the combined coherent and incoherent scattering of the solute and solvent. The coherent and incoherent scattering contributions of a 12 mM aqueous solution of PtPOP is shown in Figure 3.11.

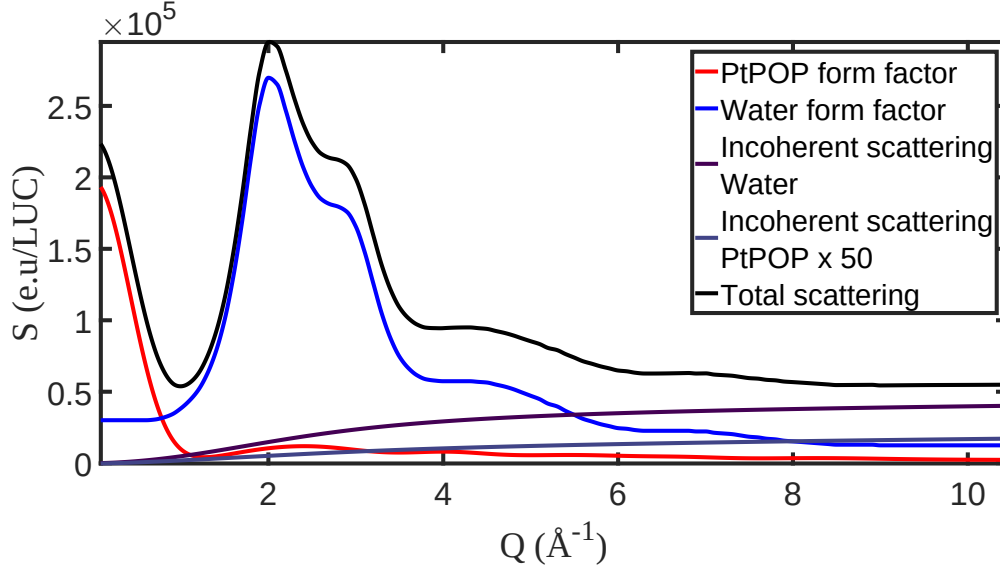


Figure 3.11: The theoretical scattering contributions of a 12 mM aqueous solution of PtPOP.

3.2.3 Correcting for X-ray Energy and Intensity

As seen from Eq. 2.4 the scattering vector, Q , is a function of X-ray energy. As such the X-ray scattering from two different X-ray energies will be mapped differently on the detector. Thus, a broad distribution in X-ray pulse energies will result in a smearing of the scattering signal. However, for each scattering signal the X-ray pulse energy is recorded and the smearing may be reduced by correcting for the fluctuations in X-ray pulse energy. In addition, the CSPAD detector has a nonlinear response to the X-ray intensity which may also be corrected using the intensity diagnostics. In [26] an SVD-based procedure of how to correct for the detectors response for non-linearities in X-ray energy and intensity is described. This procedure was paramount for the success of previous TR-WAXS studies using the first version of the CSPAD [32, 33]. The CSPAD has since been improved and the detector related artefacts have been reduced allowing for a more uniform detector behaviour. The increased stability of the CSPAD enables the option to move away from the computational heavy (and outlier sensitive) 2D SVD-based approach and instead correct the 1D scattering curves for X-ray energy and Intensity. In the data reduction of [IV,VIII,IX], the scattering curves are corrected for the variation in X-ray energy in the following manner:

- Identify the laser off scattering curves.
- Bin the curves into 20 X-ray Energy bins and take the average of each bin. This gives a matrix of the laser off scattering signals as function of Q points and X-ray Energy.
- Create a correction matrix. Accomplished by taking the Energy resolved laser-off scattering matrix and subtracting the (Energy) average of the entire matrix.

This correction matrix contains how the scattering curves vary from the average as a function of Energy.

- Apply the X-ray energy diagnostics in conjunction with the correction matrix to individually correct each scattering curve.

In a similar fashion the scattering curves may be corrected for X-ray intensity. The left hand side of Figure 3.12 shows X-ray energy correction matrix and on the right hand side the Intensity correction matrix is shown.

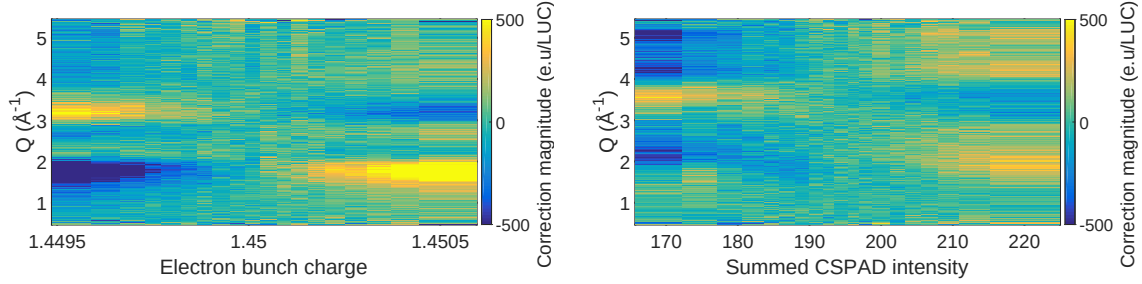


Figure 3.12: The X-ray energy and intensity correction matrices as calculated for the 14th azimuthal slice of [VIII] Left: The X-ray energy correction maxtrix. Right: The X-ray intensity correction matrix

3.2.4 Difference signals and time binning

After the outlier rejection and the various corrections of the data the measured scattering signals can be divided into two: Scattering signals where the optical laser initiated the photochemistry of the sample (S_{on}) and scattering signals where the optical laser never interacted with the sample (S_{off}). From S_{on} and S_{off} the laser-induced structural change of the system is contained in their difference, ΔS which is constructed as

$$\Delta S = S_{on} - S_{off}. \quad (3.5)$$

S_{off} is commonly measured periodically throughout the experiment and helps to minimize systematic errors arising from drifts in the experimental conditions. Additionally the S_{off} signal in a given ΔS is the average of the two S_{off} which are the nearest in time from the measured S_{on} .

Each of the constructed of the ΔS are time stamped using the XPP timing tool [17]. The information of the shots time of arrival is used to sort the ΔS into time bins. The temporal width of the bins depends on the given experiment (typically ranging from 10 fs - few hundreds of fs). The time sorted ΔS is often viewed as a colormap with the amplitude of the ΔS shown as a color and with axes of scattering vector (Q) and time (ΔT) (i.e the time relative to the initiation of the photochemistry of the experiment). As an example Figure 3.14 left hand side shows the isotropic ΔS as is analysed in

[VIII]. As described in 3.1.4 the 2D scattering patterns are integrated into a number of azimuthal bins. For each azimuthal bin a ΔS matrix is constructed. These matrices are used to separate the measured scattering signal into an isotropic and an anisotropic part. This further elaborated in the following section.

3.3 Laser induced anisotropy in TR-WAXS

The optical laser used initiate the photochemistry of the system in a in TR-WAXS experiment is linearly polarized. Solute molecules oriented such that they have a transition dipole moment on axis with the polarisation vector of the optical laser, have a higher probability of absorbing a photon. This gives rise to solute molecules in the solution being preferentially excited based on their orientation, in relation to the polarisation of laser. This results in an excited state molecular ensemble with a $\cos^2$ distribution of molecular geometries [31]. However, as the molecules are in constant motion the distribution of the excited state ensemble is diminished on the time scale of rotational diffusion of the solute molecules. The time scale of rotational diffusion depends on the size of the molecule but typically ranges from 10-200 ps. Thus, on femtosecond time scale, accessible from XFEL's, the X-ray scattering of the excited state ensembles is no longer isotropic but instead anisotropic (azimuthally dependant). The formalism necessary for the analysis of asymmetric scattering patterns and the information gained from anisotropic scattering has been treated in [34], [II] and used in [32, 33], [VIII, X]. In [34], [II] it is shown that the scattering from oriented ensemble contains information on both the isotropic and anisotropic scattering and can be separated into the isotropic contribution,

$$S_0(Q) = c_0 \sum_{i,j}^N f_i(Q) f_j(Q) \frac{\sin(Qr_{ij})}{Qr_{ij}}, \quad (3.6)$$

and into the anisotropic contribution,

$$S_2(Q) = c_2 \sum_{i,j}^N f_i(Q) f_j(Q) P_2(\cos \theta_{ij}) j_2(Qr_{ij}), \quad (3.7)$$

where c_0 and c_2 defines the relative magnitude of the isotropic and anisotropic contributions and r_{ij} is the inter-atomic distances. P_2 is a second order Legendre polynomial, θ_{ij} is the angle between the laser polarisation axis and the scattering vector and j is the second order spherical Bessel function.

In praxis the S_0 and S_2 contribution is found from data through a linear fit. For each scattering angle the given azimuthal data points are projected onto the $P_2 \cos(\theta_{ij})$ function and a linear fit using Theil-Sen Regression is made. The procedure is demonstrated for a ΔS scattering pattern of PtPOP in Figure 3.13.

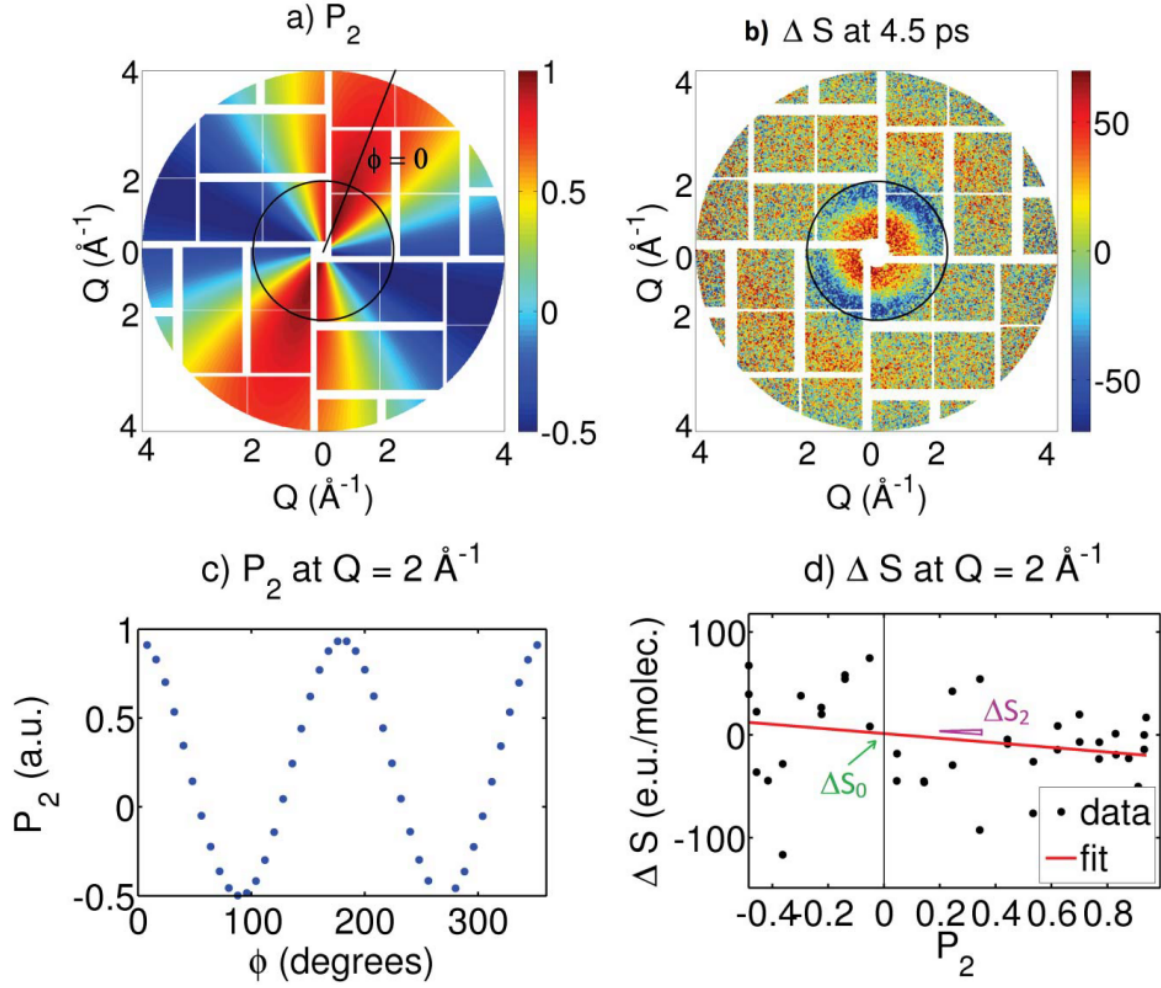


Figure 3.13: a) P_2 ($\cos(\theta_Q)$), with $\cos \theta_Q = -\cos \theta \cos \phi$, mapped on the CSPAD. The azimuthal angle ϕ is defined to be zero at the projection of the laser polarization axis on the detector surface. A radial bin corresponding to $Q = 2 \text{ \AA}^{-1}$ is selected. b) Averaged difference scattering pattern at 4.5 ps after photoexcitation of PtPOP in water. c) Value of P_2 for the specific radial bin selected in panel (a) as a function of azimuthal angle ϕ , corresponding to $Q = 2 \text{ \AA}^{-1}$. d) Difference scattering signal ΔS at $Q = 2 \text{ \AA}^{-1}$ versus P_2 (black dots) and fitted straight line (red). The intercept with $P_2 = 0$ yields the isotropic scattering signal and the slope yields the anisotropic scattering signal. From [II]

As indicated in column (d) of the figure the intersection at $P_2 \cos(\theta_{ij}) = 0$ gives the S_0 contribution while the slope of the linear fit provides the S_2 contribution.

As an example of the difference in the shape of isotropic and anisotropic scattering Figure 3.14 shows the isotropic and anisotropic difference scattering signals of the experimental data obtained in relation to [VIII].

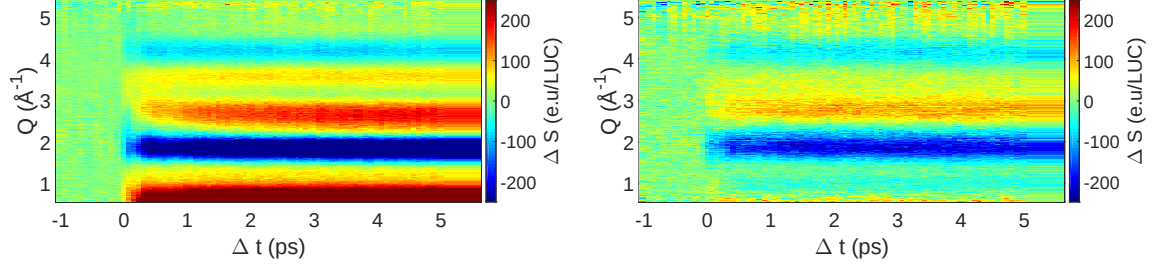


Figure 3.14: The difference scattering signals of TIPtPOP in aqueous solution. Left: The isotropic contribution. Right: The anisotropic contribution

Having outlined important elements in data production procedure, the thesis will now present the results of two XFEL studies where the associated data reductions were performed using the considerations presented in this chapter.

The photo-fragmentation cycle of $\text{Ru}_3(\text{CO})_{12}$

4

This chapter summarizes a (2016) XFEL study [IV] on the photo-fragmentation life cycle of triruthenium dodecacarbonyl ($\text{Ru}_3\text{CO}_{12}$). $\text{Ru}_3\text{CO}_{12}$ is a triangular metal carbonyl complex as illustrated in Figure 4.1.

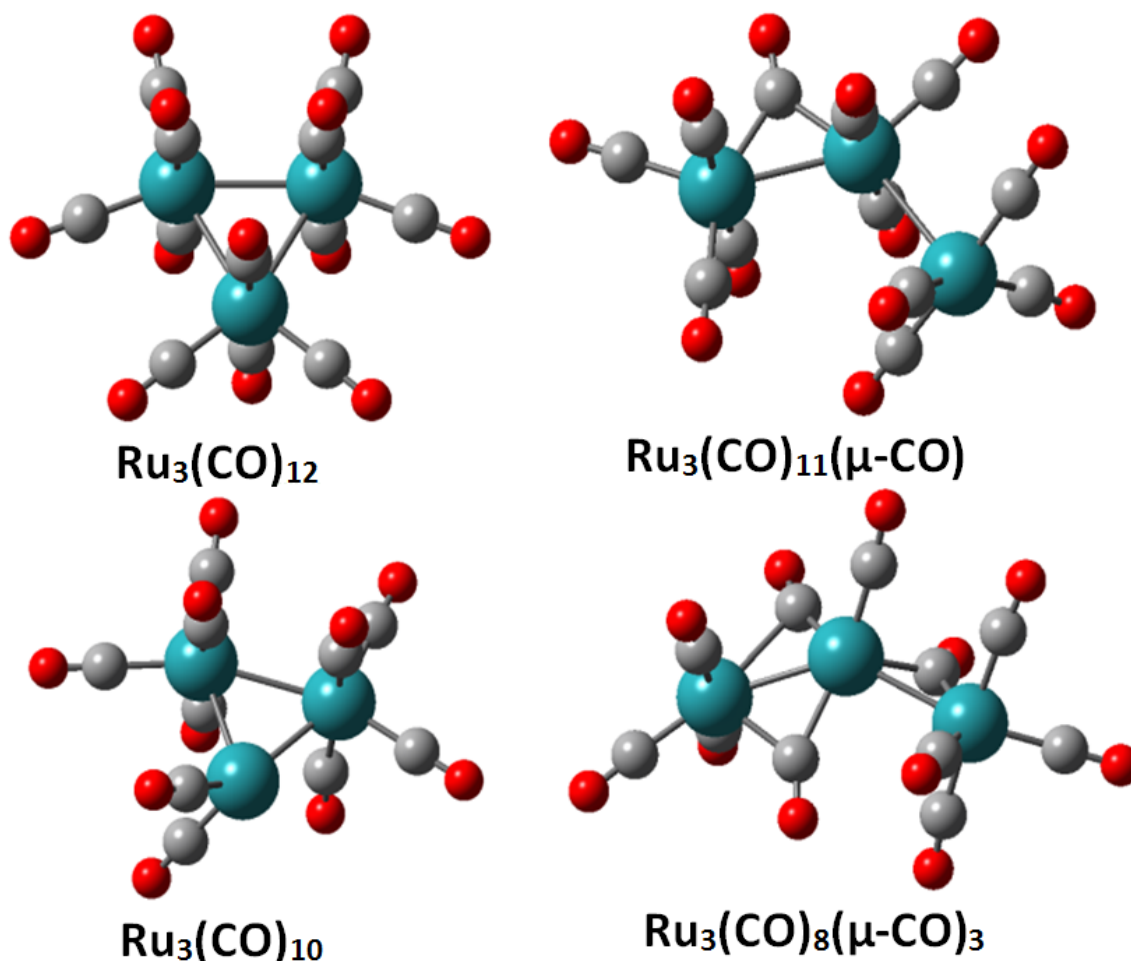


Figure 4.1: The ground state structure (top left) and transient structures found in the analysis of [IV]. Ru: cyan, C: gray, O: red.

The interest in $\text{Ru}_3(\text{CO})_{12}$ originates partially from its catalytic properties e.g its ability to function in light driven isomerization processes [36, 37] and its nitrile (RCN) reduction functionality [38]. To understand why $\text{Ru}_3(\text{CO})_{12}$ exhibits these properties both optical [35–37, 39] and X-ray studies [40, 41] have been performed. The studies identified a rich photo-fragmentation life cycle following irradiation of $\text{Ru}_3(\text{CO})_{12}$ with UV or visible light, and the transient structures of this photo-fragmentation are still debated in the literature. Using the combination of UV-vis pump ultrafast infrared spectroscopy and DFT modelling the authors of [39] identified several intermediate structures and proposed two unique fragmentation mechanisms for pump wavelengths of 266 nm and 400 nm respectively. However, UV-vis pump ultrafast infrared spectroscopy is primarily sensitive to the optical signatures of bridging carbonyls in the intermediate structures, meaning that intermediates without bridging carbonyls might have been overlooked. Therefore the optical studies were expanded by TR-WAXS experiments, since almost all potential intermediate structures have unique X-ray scattering signals. The TR-WAXS studies were conducted by Kong et al. in [40] and [41] the first of which studied the photo-fragmentation of $\text{Ru}_3(\text{CO})_{12}$ with the initiation of the life cycle using a laser-pump wavelength of 390 nm and in the latter the life cycle was studied using a laser-pump wavelength of 260 nm and 390 nm. Both studies confirmed the existence of a non-bridging carbonyl intermediate being a major photoproduct in the $\text{Ru}_3(\text{CO})_{12}$ life cycle. However, one of the bridging carbonyls intermediates confirmed by [39] could not be confirmed from the structural analysis of the TRWAXS data showing the need for complementary spectroscopy techniques. Additionally, as [40, 41] were conducted at synchrotron facilities with an intrinsic time-resolution in the tens of picoseconds regime, the earliest scattering signal of the photo-fragmentation that could be recorded was at a time delay of 42 ps. The dominant intermediate structure identified at this earliest time delay was a $\text{Ru}_3(\text{CO})_{10}$ structure which has undergone loss of two CO groups. It is unlikely that this intermediate is formed directly as the result of a single photon absorption event, as this would require simultaneous loss of both CO groups. Rather successive CO loss in the first 42 ps is more intuitive. However, Synchrotrons have insufficient time resolution needed to resolve such a two-step reaction mechanism for the CO loss.

Resolving the kinetics of the earliest intermediates formed in the photo-fragmentation of $\text{Ru}_3(\text{CO})_{12}$ requires the time resolution of an XFEL and in June of 2016 we conducted such a TRWAXS experiment at the XPP end station of the LCLS XFEL. The specifics of the experiment and the associated data reduction is presented in the following section after which the results of the experiment is presented and discussed.

4.1 The TR-WAXS experiment and data reduction

This section briefly describes the specifics of the $\text{Ru}_3(\text{CO})_{12}$ experiment and some of the challenges faced in performing the data reduction of the experiment.

The TR-WAXS experiment was conducted over three 12 hour shifts at the XPP beamline of LCLS. For each experimental day a fresh 2 mM sample of $\text{Ru}_3\text{CO}_{12}$ in cyclohexane was prepared every sixth hour in order to minimize possible sample degradation. The principles of a TR-WAXS experiment is described in Section 2.3. Specifically for the experiment we used a capillary nozzle of 100 μm in diameter and a flow speed of 1.5 ml/min (3 mm/s). The optical laser system at the XPP station of LCLS provided 14 μJ laser-pump pulses at 400nm with a temporal pulse profile of 30 fs fwhm. The spot size of the optical pulse and X-ray pulse were both $\approx 100 \mu\text{m}^2$ and their temporal width were both ≈ 30 fs.

The measured XDS data was extracted and reduced with the considerations presented in Chapter 3 of the thesis. Briefly reiterating, for the sake of specificity of this experiment, the 2D XDS patterns of laser-pumped/unpumped $\text{Ru}_3(\text{CO})_{12}$ in cyclohexane were recorded on the CSPAD detector [24]. For every 7th shot the XDS pattern was recorded for the unpumped system of $\text{Ru}_3(\text{CO})_{12}$ in cyclohexane and was used in the creation of the XDS difference signals as described in Section 3.2.4. Each XDS pattern is corrected for solid angle, detector efficiency and X-ray polarization effects. In addition, as the experiment was run in monochromatic mode it was of paramount importance to common mode correct the detector, a procedure that reduces common mode related fluctuations in the detector readout values. Bad pixels and shadowed regions of the CSPAD detector was removed using a mask. Subsequently the 2D scattering patterns were azimuthally integrated into 11 slices each covering an angle span of $\approx 32.5^\circ$ on the detector, generating 11 $S(Q)$ scattering curves for every X-ray shot.

Common mode correction of the data introduced a component in the measured signals that scaled non-linearly with the intensity of the individual X-ray shots. This component was removed using the procedure described in Section 3.2.3. The intensity corrected $S(Q)$ were scaled to the theoretical scattering of a liquid unit cell of a 2mM solution of $\text{Ru}_3(\text{CO})_{12}$ in cyclohexane in the Q -region of 0.7-4.0 $\text{\AA}$. Scaling to the liquid unit cell enables the extraction of solute excitation fraction and temperature increase of the solvent. An average of the 6 nearest unpumped XDS signals was subtracted from each XDS $S(Q)$ curve to create the XDS difference signals, $\Delta S(Q)$. Each $\Delta S(Q)$ was time stamped using the XPP timing tool [19] and sorted into time bins with ≈ 2000 curves in each bin. The $\Delta S(Q)$ curves in a given time bin were averaged after being subject to outlier rejection based on the in-set median of the $\Delta S(Q)$. Through the outlier rejection 10-20% of the curves were discarded. This procedure was carried

out for each of the 11 $S(Q,t)$ giving 11 $\Delta S(Q,t)$. Using the 11 $\Delta S(Q,t)$ the signal was separated into an isotropic and anisotropic component as described Section 3.3. The isotropic and anisotropic signal is shown for the first 10 ps in Figure 4.2.

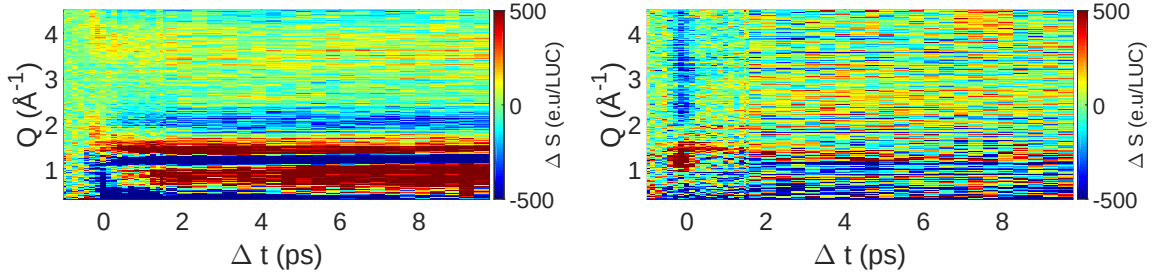


Figure 4.2: The first 10 ps of the isotropic (left) and anisotropic part (right) of the measured difference signal.

The ultrafast component seen in the anisotropic signal close to $\Delta T = 0$ likely arises from the optical Kerr effect, i.e the transient response of the solvent molecules to the electric field of the laser pulse, as is seen for the case of water [42].

There were several challenges in relation to the data correction and reduction. The major issue was that the difference signal was on the order of a few per mill in relation to the full scattering signal which emphasized the need for robust outlier rejection. The relatively weak difference signal originated in the combination of a low 2mM sample concentration and a low excitation fraction due to the temporally short optical pulse. Additionally, as the experiment was conducted using monochromatic X-rays the number of photons per X-ray pulse was substantially reduced compared to typical XFEL TR-WAXS experiments providing a significantly lower signal to noise ratio than usual.

As described in Section 3.1.5 determining the correct detector distance is important as it in turn determines the Q -axis of the difference signal. The importance is further emphasized for Cyclohexane as the solvent heat differential signature has a sharp feature at $\approx Q = 1.28$ as shown in Figure 4.3. A small change in the position of this feature could potentially, be described in a structural analysis by over fitting with additional intermediate structures.

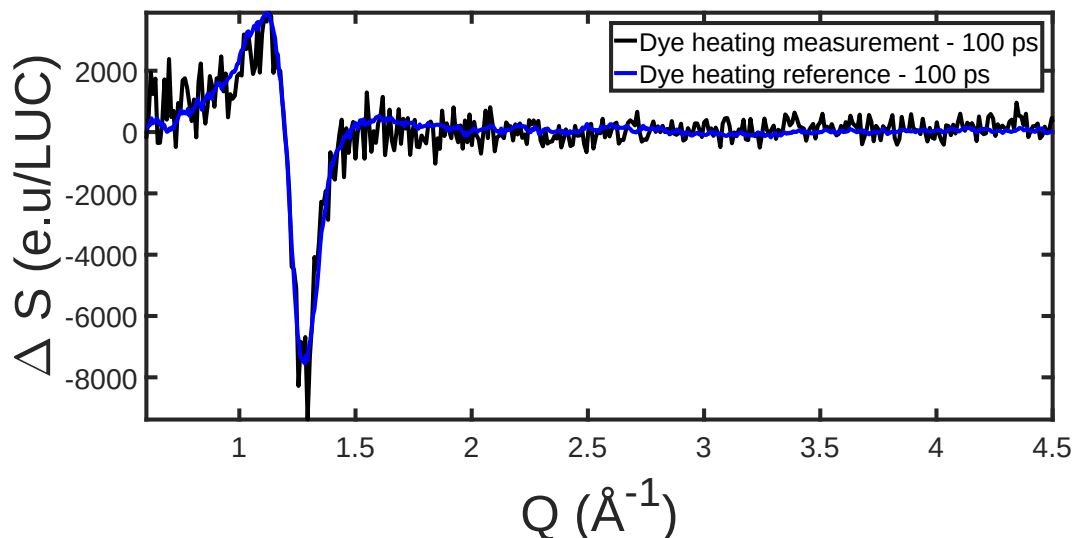


Figure 4.3: Comparison of the measured heat signature of Cyclohexane with the reference measurement of [23].

Figure 4.3 illustrates how the correct detector distance was set through the comparison of the measured heat signature of Cyclohexane and the reference measurement of [23].

As mentioned in the start of the chapter the earliest difference scattering signal obtained in previous studies was at the time delay 42 ps. It was therefore decided to measure the scattering for the first 50 ps of the photo fragmentation life cycle. The associated reduced data is presented and discussed in the next section.

4.2 Results and dicussion

The structural analysis of the obtained $\Delta S(q, t)$ is based on the fitting procedure described in Section 2.5. In the presentation of data and model both are multiplied by q for clarity of presentation. For each time delay the data was fitted with a linear combination of the difference scattering signal of the DFT-calculated intermediate structures presented in Figure 4.1, their respective cage difference signals (calculated from MD simulations) and the solvent heating signal. This routine is exemplified in Figure 4.4 where the experimental ΔS at a time delay of 5.16 ps is shown along with the best-fit theoretical model and the associated model contributions of the solute, cage and solvent.

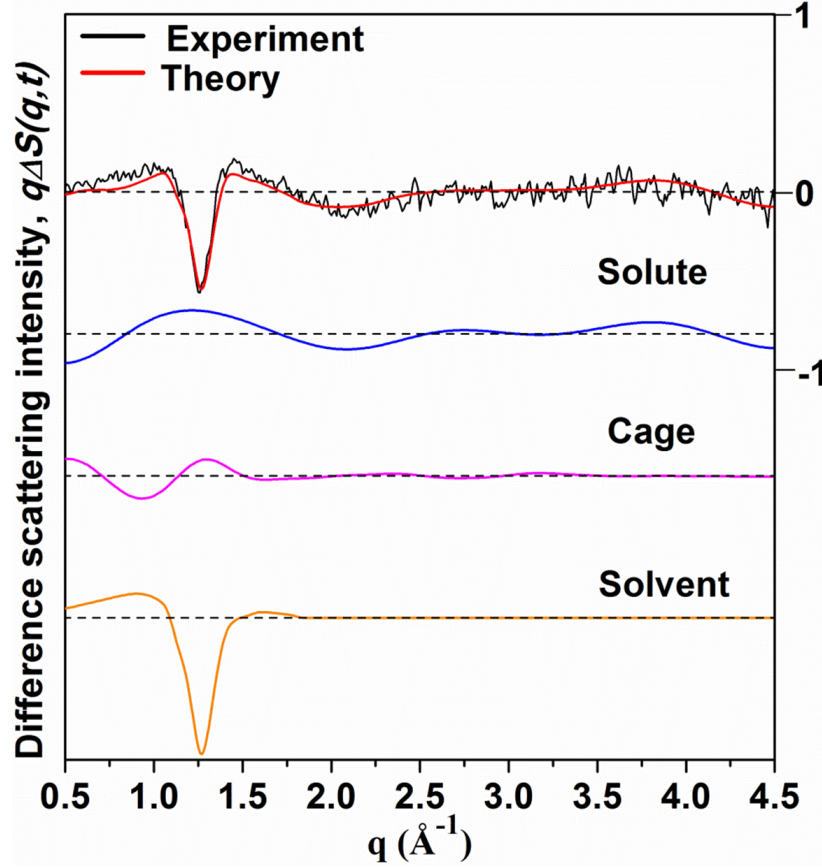


Figure 4.4: The experimental ΔS 5.16 ps after excitation and the associated best fit model (red curve). The model consist of the three contributions; The solute (blue curve), the cage (magenta curve) and the solvent contribution (orange curve)

The solvent heating signal was obtained by measuring the difference scattering signal following excitation of a purpose-synthesized sub picosecond lifetime azo-dye dissolved in neat Cyclohexane. The difference scattering signal of the intermediate structures were obtained by subtracting the theoretical scattering of the ground state structure of $\text{Ru}_3(\text{CO})_{12}$ from the theoretical scattering of each intermediate structure, i.e $\Delta S_{\text{intermediate}} = S_{\text{intermediate}} - S_{\text{Ru}_3(\text{CO})_{12}}$. Sixteen intermediate structures (shown in the SI of [IV]) based on DFT calculations were considered and tested through fitting. The four intermediate structures shown in Figure 4.1 were found to be necessary to describe the experimental data while the rest did not and thus were discarded. Figure 4.5 shows the reduced experimental data obtained for the time delay of 100 fs and 5.16 ps as well as the model fits of the most likely intermediate structures.

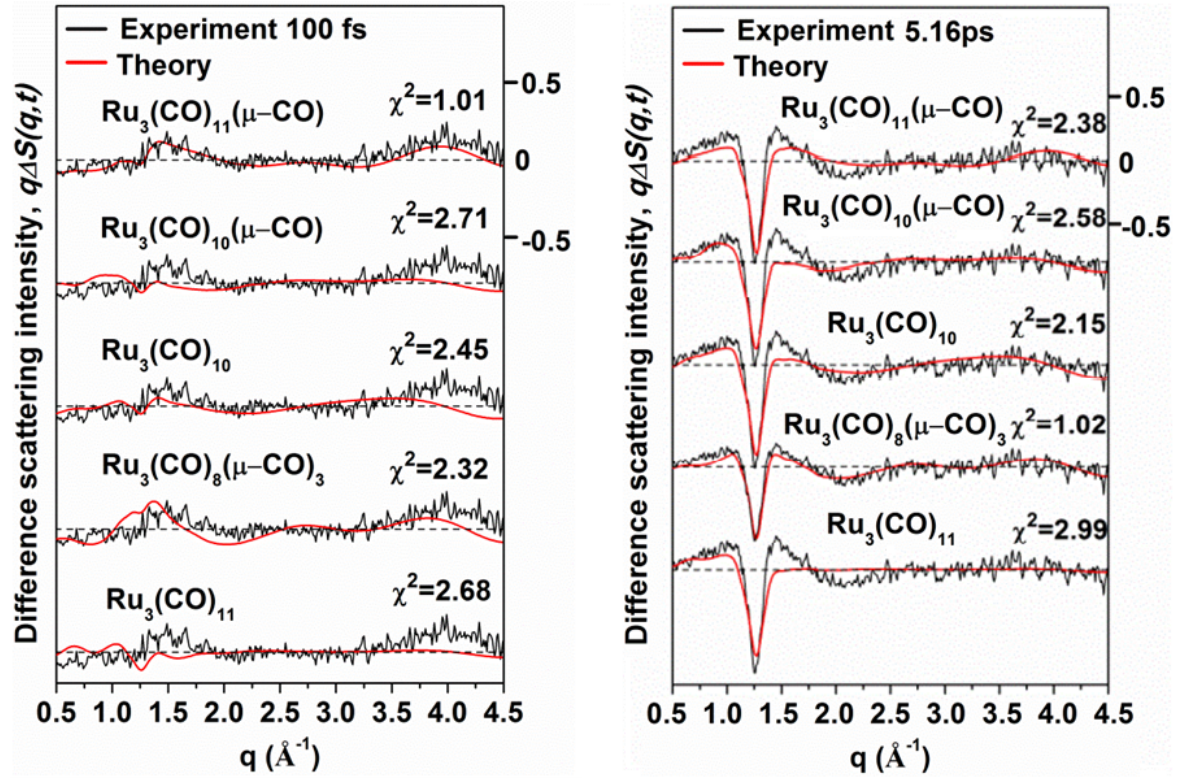


Figure 4.5: $q\Delta S(q,t)$ (black) compared with the simulated difference signal (red) of individual candidate molecular structures used in the linear combination fit. Left: 100 fs after excitation. Right: 5.16 ps after excitation.

Through the individual fitting of the ΔS for each time delay the temporal evolution of the excitation fraction of the intermediates is found. The time-evolution of the excitation fraction of the identified transient species is illustrated by the scatter plot in Figure 4.6. This evolution provides a means for quantifying the reaction mechanism of the initial steps in the photo fragmentation cascade as discussed in the following.

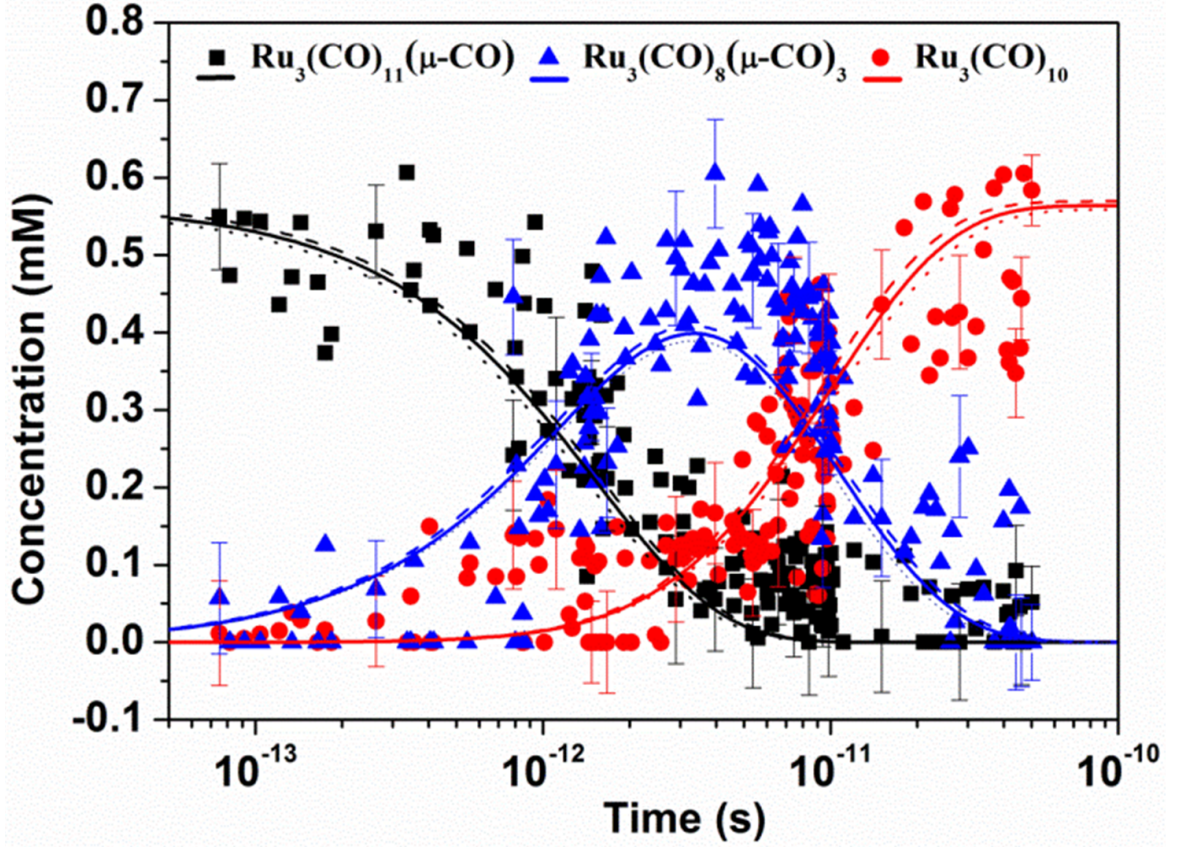
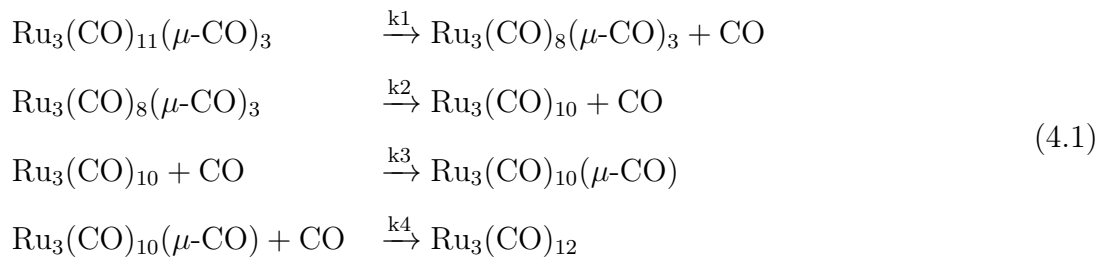


Figure 4.6: Evolution of the population of transient species as a function of time: $\text{Ru}_3(\text{CO})_{11}(\mu\text{-CO})$ (black), $\text{Ru}_3(\text{CO})_{11}(\mu\text{-CO})_3$ (blue) and $\text{Ru}_3(\text{CO})_{10}$ (red). Scatter plots are the result of the analysis of individual time delays while the solid curves correspond to global fitting. The dashed and dotted lines represent the time course of the concentrations for reaction rate constants on two sides of the 95% confidence level. Error bars obtained from the standard deviations of the experimental data are shown for one out of ten time points only for clarity. The maximum concentration of $\text{Ru}_3(\text{CO})_{11}(\mu\text{-CO})_3$ (0.56 mM) corresponds to 28% conversion in the photolysis.

The first intermediate formed after excitation of $\text{Ru}_3(\text{CO})_{12}$ is $\text{Ru}_3(\text{CO})_{11}(\mu\text{-CO})$. This intermediate transforms into $\text{Ru}_3(\text{CO})_8(\mu\text{-CO})_3$ which in turn transform into $\text{Ru}_3(\text{CO})_{10}$. Using this model the kinetics is found from global analysis where we construct a kinetic model based on the following four reactions:



Solving the associated rate equations of the above reactions (SI of [IV]) generates the kinetic model shown as the full drawn curves of Figure 4.6 with the dashed and dotted

curves representing the 95% confidence interval. From the global analysis a reaction mechanism for the first 50 ps can be produced and in combination of previous X-ray studies a full reaction mechanism can be proposed and is illustrated in Figure 4.7.

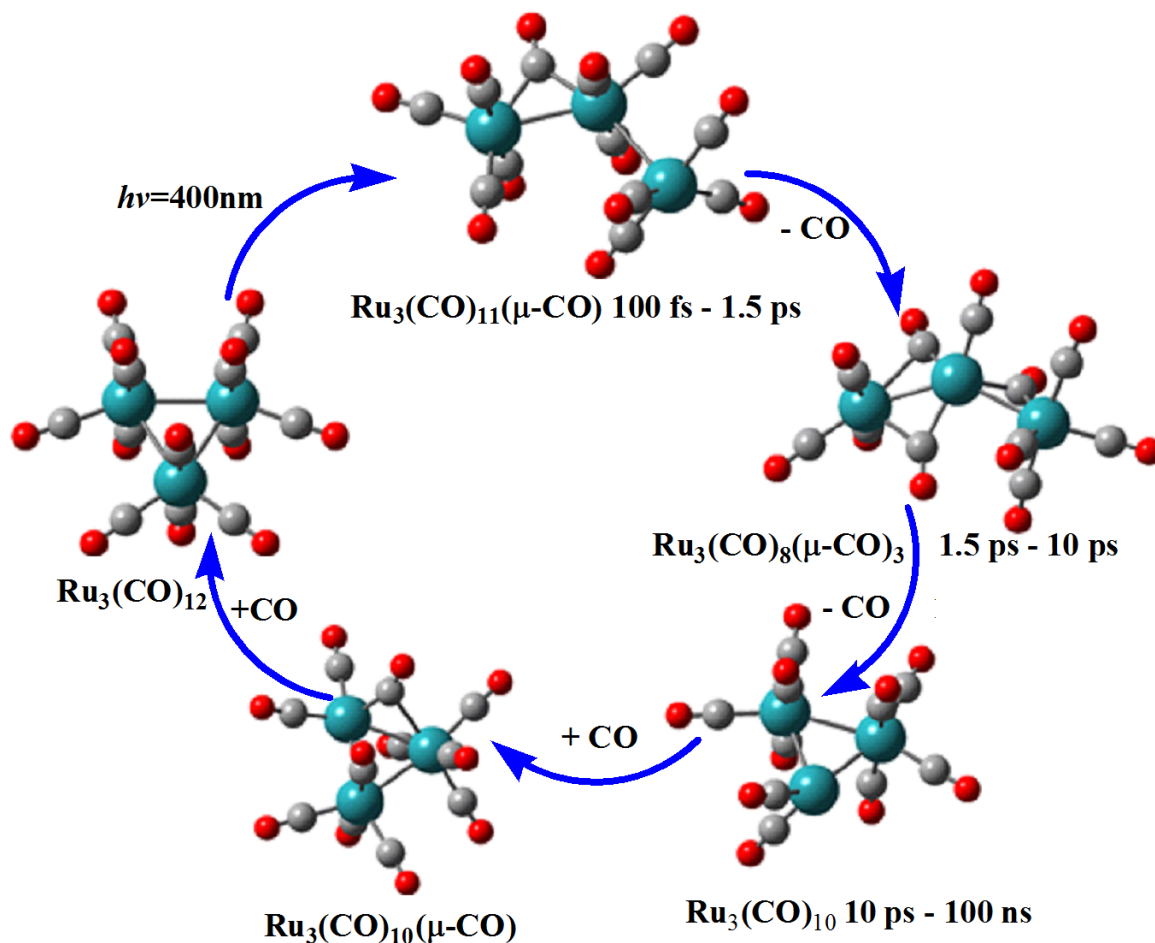


Figure 4.7: Reaction pathway of photofragmentation of $\text{Ru}_3(\text{CO})_{12}$ in C_6H_{12} following 400 nm excitation. Laser excitation breaks one Ru-Ru bond to form $\text{Ru}_3(\text{CO})_{11}(\mu\text{-CO})$, which loses one CO to form $\text{Ru}_3(\text{CO})_8(\mu\text{-CO})_3$ at 1.5 ps. The latter loses another CO and yields $\text{Ru}_3(\text{CO})_{10}$ at 10 ps. $\text{Ru}_3(\text{CO})_{10}$ dominates from 10 ps to 100 ns, and rebinds one CO to form $\text{Ru}_3(\text{CO})_{10}(\mu\text{-CO})$ which eventually relaxes to the starting molecule by binding another CO. Ru: cyan, C: gray, O: red.

As can be seen from the Figure we propose that at the onset of the reaction the absorption of 400 nm photon leads to a breakage of a Ru-Ru bond and the carbonyl bridged structure, $\text{Ru}_3(\text{CO})_{11}(\mu\text{-CO})$, is formed. This intermediate is the dominant species in the first 1.5 ps after which the structure loses a carbonyl and the triple bridged CO intermediate, $\text{Ru}_3(\text{CO})_8(\mu\text{-CO})_3$ is formed and is the dominant species between $\approx 1.5 - 10$ ps. With the loss of another carbonyl group $\text{Ru}_3(\text{CO})_8(\mu\text{-CO})_3$ forms the terminal carbonyl intermediate, $\text{Ru}_3(\text{CO})_{10}$. Based on previous studies [40, 41] this intermediate lives for up to ≈ 100 ns after which combines with a carbonyl group to form the intermediate, $\text{Ru}_3(\text{CO})_{10}(\mu\text{-CO})$ [39]. This last intermediate eventually re-

laxes to the ground state structure through the addition of another carbonyl group.

The discovery of the intermediate, $\text{Ru}_3(\text{CO})_8(\mu\text{-CO})_3$, immediately raises the question as to why IR studies did not suggest its existence. This could be explained from the IR-signatures of the single bridged and triple bridged structures having overlapping features and thus being difficult to discern.

Additionally, the analysis confirms the existence of $\text{Ru}_3(\text{CO})_{11}(\mu\text{-CO})$. The existence of which was seen in optical studies but could not be confirmed in previous synchrotron X-ray studies and can now be understood in the light of its short ≈ 1.5 ps life time.

The present study and the previous Synchrotron studies both find $\text{Ru}_3(\text{CO})_{10}$ to be the dominant intermediate at 50 ps. This neatly ties the results of the present studies together with existing literature which, when combined, provides a complete picture of the photofragmentation of $\text{Ru}_3(\text{CO})_{12}$.

The PtPOP systems 5

This chapter presents results from our 2015 XFEL experiment where we studied the di-platinum anion $[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]^{4-}$ (abbreviated PtPOP) and its sister metal coordinated complexes, Tl-PtPOP and Ag-PtPOP. The three systems are shown in Figure 5.1.

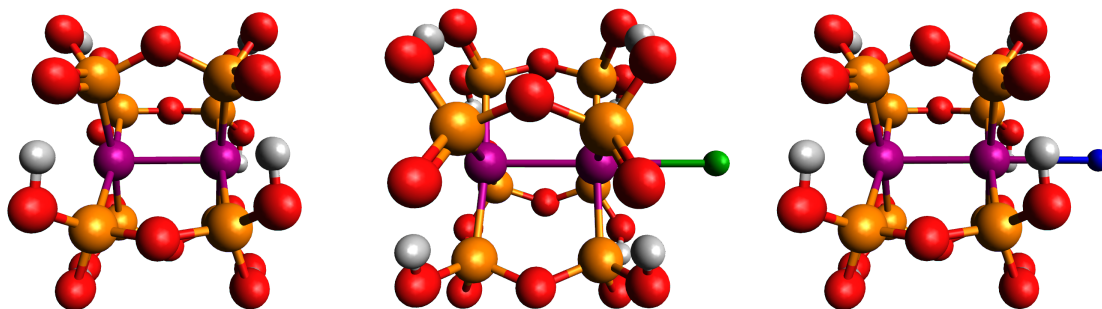


Figure 5.1: The molecular geometries of PtPOP and metal coordinated PtPOP. The different elements is represented by colour: Phosphor (orange), Oxygen (red), Hydrogen (white), Platinum (purple), Thallium (green) and Silver (blue). Left: PtPOP. Middle: Tl-PtPOP. Right: Ag-PtPOP.

The results related to PtPOP is presented in [VII] and results related to Tl-PtPOP is presented in [VIII]. The primary focus of the chapter will be the study of Tl-PtPOP.

Tl-PtPOP

The interest in Tl-PtPOP is largely connected to the naked PtPOP molecule. Decades ago it was established that upon irradiation of PtPOP with 385 nm light enters an excited state through the promotion of an electron which initially is in an anti bonding orbital [7, 43]. In its promotion it forms a bonding orbital which is located between the Pt atoms. This in turn causes a contraction in the bond length between the two Pt atoms. The Pt atoms are surrounded by a phosphorous ligand structure which effectively isolates the Pt atoms and this combined with the highly harmonic energy potential of PtPOP enables the observation of long lived coherent oscillations in transient absorption (TA) measurements [44]. The formation of a bonding orbital in excited

state PtPOP has the added effect of transferring electron density away from the ends of the Pt axis. This increases the reactivity of PtPOP in its excited state and allows for the formation of complexes which only lives in the excited state (exciplexes) [50–53]. Thus PtPOP is an important model system in the study of bond formation and structural dynamics.

Some of the earliest studies on Tl-PtPOP were optical studies [50, 51]. In [50] the authors measured the emission of an aqueous solution of PtPOP changed as thallium ions were added. The addition of thallium ions resulted in the appearance of two new emission bands. The first emission band was assigned to the formation of the axially coordinated thallium excited state complex Tl-PtPOP* while the second emission band was assigned to the doubly axially coordinated Tl-PtPOP*-Tl exciplex. With the addition of Tl ions the 368 nm absorption peak of PtPOP decreased which was assigned to the formation of a Tl-PtPOP ground state complex. Nagle commented in an end note that a similar behaviour was observed for Ag-PtPOP*. The suggestion of a preassociated thallium coordinated complex was further reinforced by Clodfelter [51]. Clodfelter measured the phosphorescence of Tl ions and PtPOP in ethylene glycol at 190K where diffusion should be minimal and observed the emission band previously assigned to the Tl-PtPOP* complex by Nagle. This result indicates that thallium is preassociated in the ground state with a conformational structure close to that of the excited state Tl-PtPOP* complex. While the optical studies by Nagle and Clodfelter provides evidence of the ground state complex and exciplex formation of metal coordinated PtPOP, no direct structural information can be derived from these optical studies.

The existing X-ray scattering studies of thallium coordinated PtPOP [49, 52] only address the exciplex formation ($\text{Tl} + \text{PtPOP}^*$) and thus the nature and structure of the preassociated ground state complex, suggested by the work Nagle and Clodfelter, is not well described. The following sections seeks to uncover the structure of the ground state TlPtPOP complex and its photo initiated structural dynamics.

The analysis and discussion of the photophysics of TlPtPOP is based on the combination of TA measurements and the structural analysis of TR-WAXS data. In the following section the TA measurements of TlPtPOP and PtPOP are presented and their uncovered population kinetics motivate a model for the possible reaction mechanism of TlPtPOP in aqueous solution. Following this is the structural analysis of TR-WAXS data of the first 5 picoseconds of TlPtPOP* after photo initiation.

5.1 Results and discussion

In preparation of the XFEL TR-WAXS experiment the transient absorption spectra of PtPOP and Tl-PtPOP were measured at Lund university. The principles of

transient absorption is well established and is readily used to characterize a broad class of systems as described in the review of [48]. Time traces of a TA spectrum provides information of the population kinetics and in some cases reveal the dynamics of electronic modes. Such modes can be assigned to structural dynamics of the measured system but does not directly provide any structural information. However, the information from a TA measurements is complementary to TR-WAXS data and can, when combined, help provide a more complete description of a given system.

5.1.1 Transient absorption of Tl-PtPOP

The pump wavelength used in the TA measurements of PtPOP and Tl-PtPOP samples in aqueous solution was set to 400 nm to match the pump wavelength of the TR-WAXS experiment. The absorption difference, ΔA , of laser pumped PtPOP and Tl-PtPOP samples were measured for wavelengths between 425 and 600 nm. In the left hand side of Figure 5.2 the TA spectrum of the Tl-PtPOP sample is shown. The middle of the figure shows the temporal evolution of the 440 nm ΔA data. The data have been fitted with an exponential function for the purpose of removing the slow varying temporal component from the data. Subtracting the slow varying temporal component from the data creates a residual containing the fast varying temporal components, the frequency/period of which may be revealed through a Fourier transform. The 1 to 2.5 ps snippet of the residual is convoluted with a hanning window and Fourier transformed by the program described in [47]. The result of the Fourier transform is shown on the right hand side of Figure 5.2.

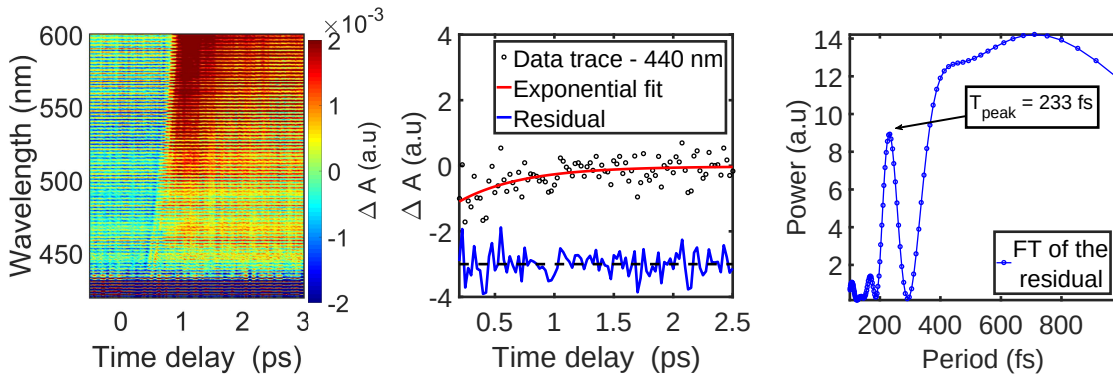


Figure 5.2: Left: Transient absorption measurement of **Tl-PtPOP** in aqueous solution. Middle: Temporal data trace at 440 nm (black dots) and exponential model fit (red curve). The residual created by subtracting the model fit from the data is shown as the blue curve. Right: The Fourier transform of the residual.

As can be seen from the figure the dominant period in the Fourier transform is centred at 233 fs. This period is close to the ~ 225 fs period of the **excited state** potential of PtPOP reported by Veen et al. [44] and can thus be interpreted as arising from the excited state Pt-Pt bond dynamics of the Tl-PtPOP complex. Figure 5.3 shows the

TA spectrum of PtPOP in solution, the temporal trace of the 430 nm wavelength and the Fourier transform of the residual.

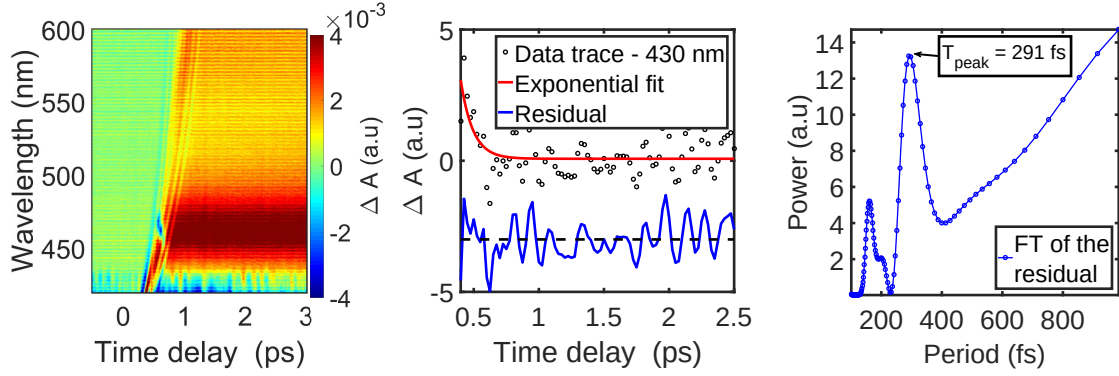


Figure 5.3: Left: Transient absorption measurement of **PtPOP** in aqueous solution. Middle: Temporal data trace at 440 nm (black dots) and exponential model fit (red curve). The residual created by subtracting the model fit from the data is shown as the blue curve. Right: The Fourier transform of the residual.

The Fourier transform reveal a dominant period centred at 292 fs. This period is close to the 280-290 fs period of the **ground state** potential for PtPOP reported previously in [44–46]. The fourier revealed periods of Tl-PtPOP (233 fs) and PtPOP (292 fs) are assigned to the structural dynamics of the systems. As such one would expect to see the same periods in TR-WAXS data (given similar time resolution).

5.1.2 TR-WAXS of Tl-PtPOP

The principles of a TR-WAXS experiment is presented in Section 2.3. The TR-WAXS experiment was conducted at the LCLS XFEL and the key paramters of the experiment is given in Table 5.1.

X-ray pump Energy	9.5 keV (0.2% bandwidth)
X-ray pulse temporal width	30 fs (fwhm)
X-ray focal spot size	$\sim 100 \mu\text{m}^2$
Laser pump wavelength	$395 \text{ nm} \pm 5 \text{ nm}$ (fwhm)
Laser pulse temporal width	80 fs (fwhm)
Laser pulse energy per pulse	$5 \mu\text{J}$
Laser focal spot size	$\sim 100 \mu\text{m}^2$
Liquid jet (circular) diameter	$100 \mu\text{m}$
Liquid jet flow velocity	$\sim 1.5 \text{ m/s}$
PtPOP concentration	20 mM
CF ₃ O ₃ STl concentration	110mM
Sample-to-detector distance	$\sim 5.1 \text{ cm}$

Table 5.1: The key parameters of our 2015 XFEL TR-WAXS experiment. The experiment was conducted at the XPP end station of the LCLS facility.

The recorded scattering data was reduced and treated as described in Chapter 3 and the resultant isotropic difference scattering is presented in the left hand side of Figure 5.4.

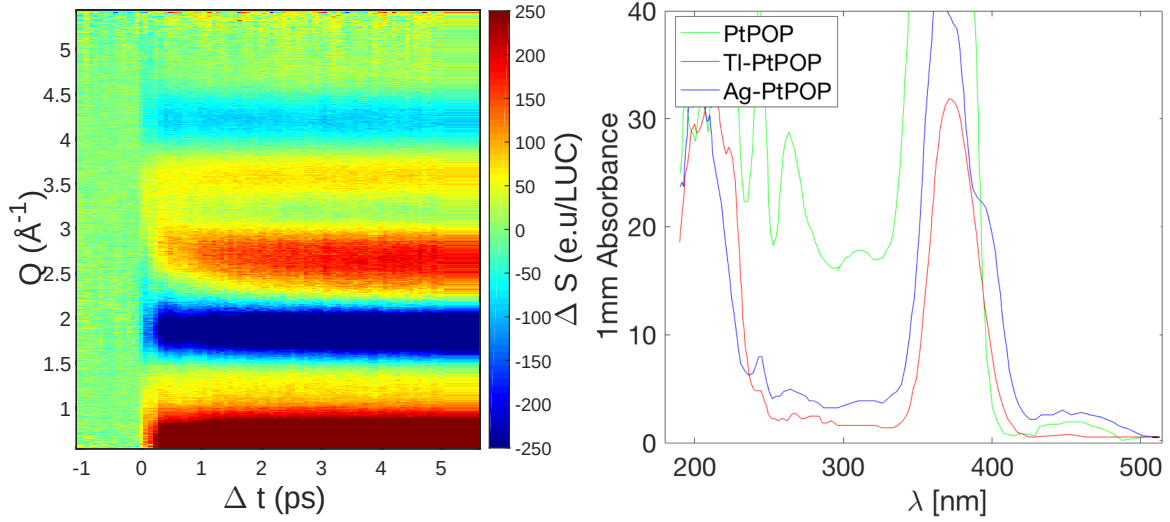


Figure 5.4: Left: The isotropic contribution to the time resolved difference scattering of Tl-PtPOP in aqueous solution. Right: The absorption spectra of PtPOP (green curve), Tl-PtPOP (red curve) and Ag-PtPOP (blue curve).

On the right hand side of the same figure the absorption spectra of PtPOP, Tl-PtPOP and Ag-PtPOP are shown. As can be seen from the figure the addition of thallium or silver metal ions to a aqueous solution of PtPOP changes the absorption spectrum. The same observation was made in [50] and was assigned to the formation of thallium and silver coordinated PtPOP in the ground state (i.e Tl-PtPOP, Ag-PtPOP).

Similarly to the study of the TA data a Fourier transformation has been used to uncover potential oscillations of the Tl-PtPOP scattering data. The power of Fourier transforming scattering data was shown in [32] where it was used to visualize the sequential activation of vibrational modes of the transition metal complex, $[\text{Co}(\text{terpy})_2]^{2+}$. This was accomplished through a time-resolved Fourier transform temporal trace at a certain scattering vector, Q , after having subtracted broadened step function convoluted with a exponential decay.

Figure 5.5 shows a temporal trace of the Tl-PtPOP $\Delta S(Q,t)$ averaged for values of Q between 0.6 and 1.5. The trace is fitted with a broadened step function and the residual created by subtracting the model form the data is shown. In the middle of the figure the Fourier transform of the residual from -1 to 5 ps is shown. On the right hand side of the figure the time resolved Fourier transform is shown. The time resolved Fourier transform is made using a "sliding" 1 ps window. The price to be paid for doing a time resolved Fourier transform is a decrease in the resolution of the frequencies/periods.

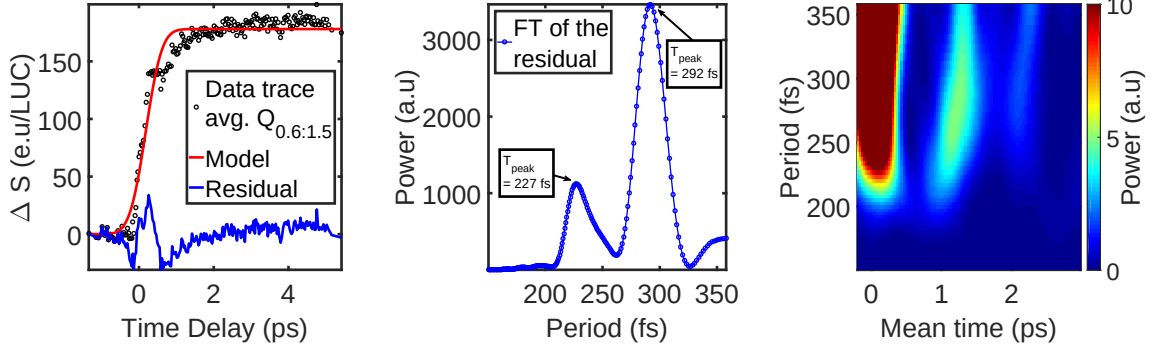


Figure 5.5: Left: The temporal trace of the $\Delta S(Q,t)$ of Tl-PtPOP averaged for values of Q between 0.6 and 1.5 (black dots). The data is modelled with a broadened step function (red curve). The residual obtained from subtracting the model from the data is shown as the blue curve. Middle: The Fourier transform of the residual. Right: The time-resolved Fourier transform of the residual using 1 ps windows.

Visible from the Figure 5.5 is that the broadened step function qualitatively does not describe data well around 0.5 ps. Despite of this the Fourier transform of the residual reveals two dominant periods centred at 227 and 292 fs. The time resolved Fourier transform is not able to reveal a clear temporal evolution the two dominant periods and is attributed to the quality of the scattering data. To address the broadens step function inability to describe data at 0.5 ps another model consisting of the combination of a broadened step function and a double exponential function (delayed 0.5 ps) is created. Similarly to the previous figure the model is compared to the $\Delta S(Q,t)$ trace as shown in Figure 5.6.

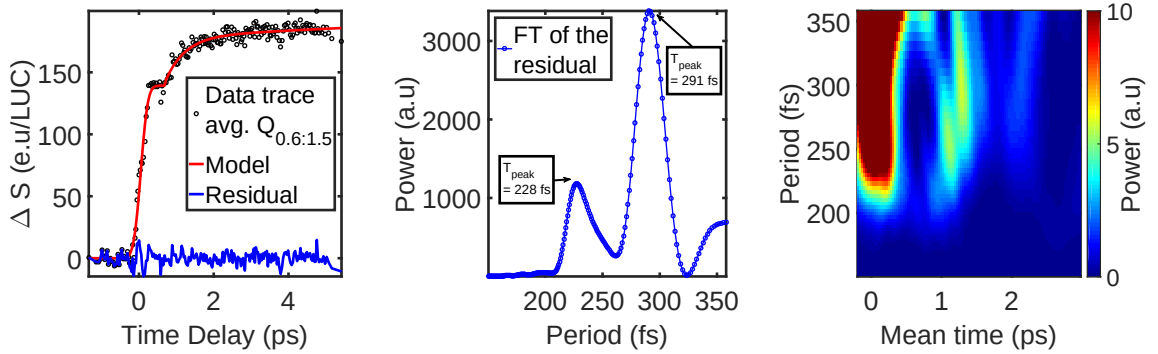


Figure 5.6: Left: The temporal trace of the $\Delta S(Q,t)$ of Tl-PtPOP averaged for values of Q between 0.6 and 1.5 (black dots). The data is modelled with a broadened step function (red curve) and a 0.5 ps delayed exponential function. The residual obtained from subtracting the model from the data is shown as the blue curve. Middle: The Fourier transform of the residual. Right: The time-resolved Fourier transform of the residual using 1 ps windows.

While the model better describes data in the entire temporal range it does not signif-

icantly affect the periods seen by the Fourier transform nor does the improved model qualitatively change the the time resolved Fourier transform.

The periods seen from the Fourier transform of the $\Delta S(Q,t)$ are in good agreement with the 233 and 292 fs TA periods seen for Tl-PtPOP and PtPOP. Thus the two dominant periods is interpreted as arising from excited state Pt-Pt bond dynamics of Tl-PtPOP and ground state Pt-Pt bond dynamics of PtPOP. The concurrent reaction of two species can be understood in light of the weak coordination between thallium ions and PtPOP molecules. As listed in Table 5.1 the concentration of $\text{CF}_3\text{O}_3\text{STl}$ in the sample was 110 mM which for a liquid unit cell translates to ~ 5.5 thallium ions per PtPOP molecule. However, at equilibrium only a fraction of thallium ions are coordinated to the PtPOP molecule. As such a concentration of 110 mM $\text{CF}_3\text{O}_3\text{STl}$ in a 20mM PtPOP aqueous solution will result in a sample in which both the Tl-PtPOP and PtPOP species are present. However, as can be seen from Figure 5.4 Tl-PtPOP have a higher probability to absorb a 395 nm photon than PtPOP which explains how the Tl-PtPOP subspecies can be visible in the scattering data.

5.1.3 Modelling Tl-PtPOP TR-WAXS data

Based on the presence of the 228 fs and 291 fs periods in the data of Tl-PtPOP the $\Delta S(Q,t)$ is modelled as the sum of the individual dynamics of Tl-PtPOP and PtPOP as given in Equation 5.1

$$\Delta S(t) = \alpha(t)\Delta S_{\text{Tl-PtPOP}}(\Delta\bar{\mathbf{R}}_1) + \Delta T(t) \left. \frac{\partial S_{\text{H}_2\text{O}}}{\partial T} \right|_{\rho} + \beta(t)[\Delta S_{\text{PtPOP}}(\Delta\bar{\mathbf{R}}_2) + \Delta S_{\text{Cage}}], \quad (5.1)$$

where the scattering vector Q has been omitted for simplicity. Here t is the time delay between the laser pump pulse and the X-ray probe pulse, ΔT is the temperature increase of the bulk solvent, α and β are the fractions of excited Tl-PtPOP and PtPOP molecules respectively and $\Delta\bar{\mathbf{R}}_x$ refers to the time-dependent changes in geometry of specimen x .

The PtPOP part of the model

The ultrafast structural dynamics of PtPOP in aqueous solution was uncovered in [IV] it was shown that it could be described by ~ 285 fs oscillation of the ground state Pt-Pt bond. As such the structural dynamics of the PtPOP subspecies in the Tl-PtPOP solution will be modelled as the previously established structural dynamics. However, the excitation fraction of the PtPOP subspecies is likely not the same as the excitation fraction found in the pure PtPOP study. Thus the excitation fraction of PtPOP is determined from modelling the 5 ps $\Delta S(Q)$ as elaborated below.

The Tl-PtPOP part of the model

The $\Delta S(Q,t)$ of Tl-PtPOP is modelled as difference in scattering between the excited state structure and ground state structure, $\Delta S_{\text{TlPt2}} = S_{\text{Tl-PtPOP,es}} - S_{\text{Tl-PtPOP,gs}}$. In several TR-WAXS studies the ground state structure of a given system is known from DFT and is fixed to a certain structural configuration while the excited state structure is allowed to vary through a parametrization of a key structural parameter. However, no ground state structure of Tl-PtPOP is known from the literature. Instead a vibrationally relaxed excited state structure is known from a combined X-ray scattering and DFT study of the excited state complex formation of $\text{PtPOP} + \text{Tl} \rightarrow \text{Tl-PtPOP}^*$ [49]. A reverse tactic of fixating the excited state structure while parametrizing the ground state configuration has been used to estimate the ground state structure. This tactic requires that the $\Delta S(Q,t)$ signal being modelled represents the $\Delta S(Q,t)$ of a vibrationally relaxed excited state. This is thought to be the case after 5 ps as the temporal evolution of the $\Delta S(Q,t)$ progresses towards a plateau as seen in Figure 5.6. Thus the ground state of Tl-PtPOP is determined by modelling the $\Delta S(Q)$ signal averaged between 4-5 ps.

Two distinct models for the ground state structure has been tested. The majority of the literature on Tl-PtPOP suggest that thallium is axially coordinated to PtPOP [49–52]. However, a gas-phase DFT study (simplified by neglecting spin orbit coupling) on sister complex, Ag-PtPOP, suggest that for Ag-PtPOP the Ag ion is coordinated perpendicular to the Pt-Pt axis outside of the phosphor cage of PtPOP. Due to the similarity of the Ag-PtPOP and Tl-PtPOP systems a model with side-on thallium coordinated PtPOP complex is tested. For both the side on coordinated and the axially coordinated Tl-PtPOP model the Tl-Pt and Pt-Pt distance are parametrized. The model parameters of α , β and ΔT were set as free parameters while the geometric parametrization of both the side-on and end-on Tl-PtPOP structures was implemented through a linearly spaced grid of possible Pt-Pt and Pt-Tl distances from 2.5 Å- 4.5 Å.

Each combination of Pt-Pt and Tl-Pt distance has a unique solution for which a χ^2 value is assigned using Equation 2.10. The side-on and end-on models with the minimum χ^2 (the best fits) are shown in Figure 5.7 left hand side. On the right hand side of the same figure the model components for the best fit solutions are shown.

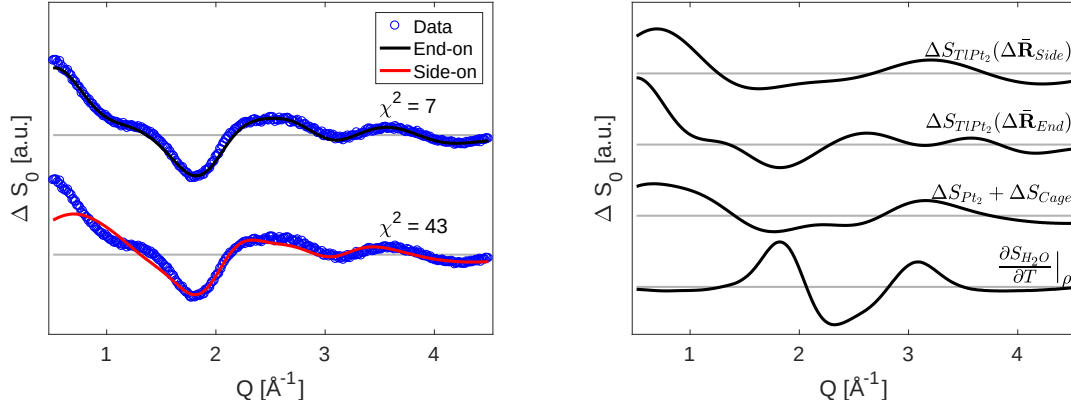


Figure 5.7: Left: A comparison of the end-on and side-on coordinated best fit models. Both models are fitted to the $\Delta S(Q)$ averaged from $t \in [4, 5]$ ps. The two model fits are offset for clarity. Right: The contributions to the $\Delta S(Q,t)$ model.

As can be seen from the figure the end-on coordinated model qualitatively describes the 5 ps $\Delta S(Q,t)$ better. A χ^2 value of 7 is computed for the end-on coordinated model while a χ^2 value of 43 is assigned to the side-on coordinated model. Thus the side-on coordinated model of Tl-PtPOP is rejected and the axially coordinated model is used for further structural analysis. From the best fit model we arrive at the excitation fractions of Tl-PtPOP and PtPOP being $\alpha = 4.81 \pm 0.03 \%$ and $\beta = 5.38 \pm 0.10\%$ respectively. The relatively large χ^2 values of 7 and 43 is thought to be an under assessment of the data related noise, $\sigma(Q)$. For the end-on ground state model we find a χ^2 minimized ground state structure with Pt-Pt = $2.94 \text{ \AA} \pm 0.32$ and Pt-Tl = $3.44 \text{ \AA} \pm 0.28$. The uncertainties estimates is found from the projection of the multidimensional $\Delta\chi^2$ contours onto the $\Delta\text{Tl-Pt}$ and $\Delta\text{Pt-Pt}$ plane as shown in Figure 5.8.

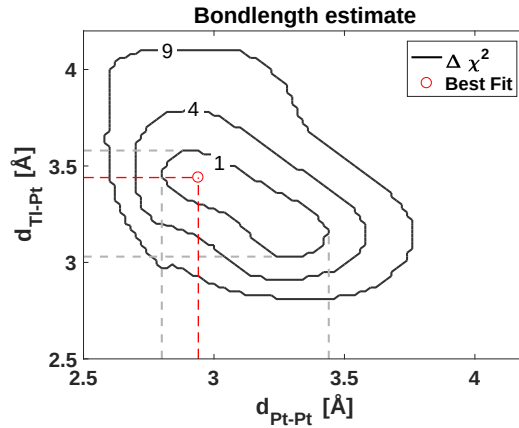


Figure 5.8: The iso-contours of the $\Delta\chi^2$ surface shown in a coordinate system spanned by the ΔPtPt and ΔTlPt structural parameters. The grey lines indicate the projection of the confidence intervals, and the red indicate the best fit value.

In the figure the $\Delta\chi^2$ iso-contours of $\Delta\chi^2 = 1, 4, 9$ corresponds to $1\sigma, 2\sigma$, and 3σ

[21, 57]. As can be seen from the elongated shape of the contours the Tl-Pt and Pt-Pt structural parameters are qualitatively anti correlated.

In the model for Tl-PtPOP no contribution from cage is included as no calculation of the cage signal exist. Part of the reason why the cage signal has not been calculated is because of the weak associative nature between thallium ions and PtPOP rendering difficulties in using DFT to predict the ground state structure. This in turn makes the calculation of the associated cage problematic as it requires the DFT structure of both the ground and excited state.. The influence of the cage signal is discussed at the end of this chapter and in the next.

Structural dynamics of Tl-PtPOP

Having found the optimized ground state structure of Tl-PtPOP the structural dynamics of Tl-PtPOP can be uncovered. This is accomplished through the structural optimization of the excited state DFT structure of Tl-PtPOP for each $\Delta S(Q, t)$. Using the model presented in Equation 5.1 each $\Delta S(Q, t)$ is fitted. In the fitting procedure the Pt-Pt and Tl-Pt bond lengths is allowed to vary freely. The excitation fractions of Tl-PtPOP (α) and PtPOP (β) is set to follow the temporal evolution of a broadened step function. Ideally the excitation fractions should appear instantaneous with regards to the XFEL time resolution but are smeared due to the instrument response function (IRF) of the experiment. Thus the temporal behaviour of α and β are in reality, $\alpha(t) = \alpha \cdot \text{IRF}(t)$, $\beta(t) = \beta \cdot \text{IRF}(t)$. The IRF can be modelled as the convolution of a Gaussian shaped pulse and a step function resulting in , $\text{IRF}(t) = 1/2 (\text{erf}((t - t_0)/\Delta t) + 1)$, where erf is the error function and Δt is the width of the Gaussian shaped pulse, estimated to a value of ~ 75 fs. The excitation fractions of Tl-PtPOP and PtPOP is set to $\alpha = 4.81 \pm 0.03$ % and $\beta = 5.38 \pm 0.10$ % as found from the ground state structural analysis.

Using this approach the number of free parameters of the Tl-PtPOP model is three, the Pt-Pt and Tl-Pt bond length of Tl-PtPOP and ΔT . The left hand side of Figure 5.9 shows the evolution of the excited state Tl-Pt and Pt-Pt bond lengths of the Tl-PtPOP* as obtained from the model fitting. On the right hand side of the figure the 2D representation of $\Delta S(Q, t)$ data is shown in the top while in the bottom the residual between the data and model is shown.

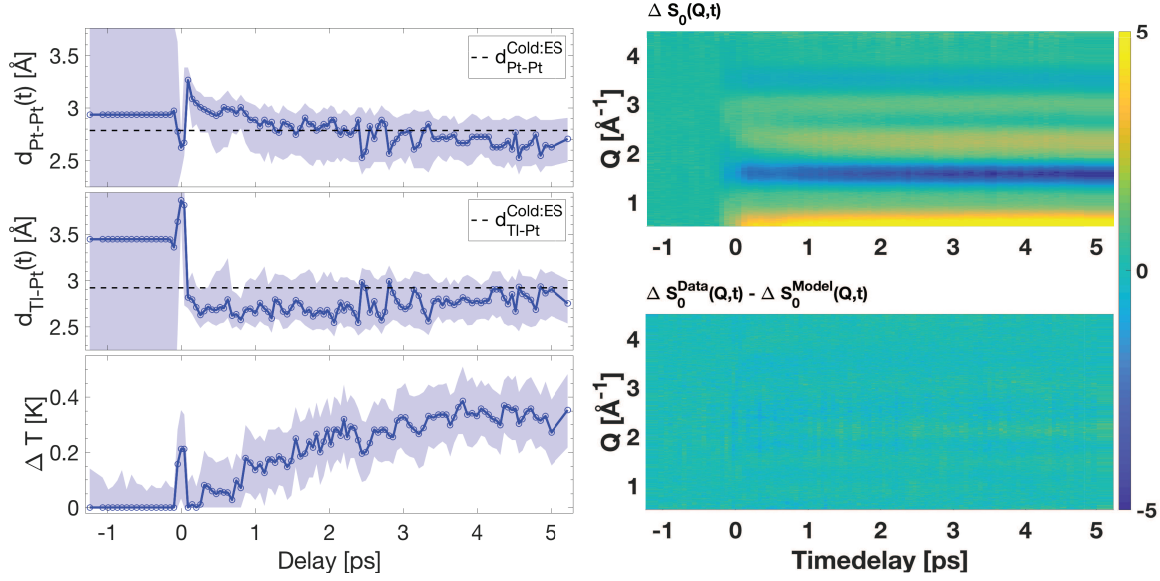


Figure 5.9: Left: The temporal evolutions of the free model fit parameters. The dashed line shows the initial values of the Tl-PtPOP DFT structure. The blue dotted curve shows the best fit model values. The shaded area is the 1σ uncertainty. Top: The change in Pt-Pt bond length. Middle: The change in Tl-Pt bond length. Bottom: The solvent temperature increase. Right: Top: The $\Delta S(Q,t)$ of Tl-PtPOP in aqueous solution. Bottom: The residual(Q,t) between the experimental data and the model. The colobar is given in e.u./molecule $\cdot 10^{-2}$.

From the figure it is seen that the model predicts an immediate contraction of the Tl-Pt distance (as compared to the ground state) after which it is relaxed towards a longer distance. The Pt-Pt distance initially increases and then proceeds to decrease to a distance shorter than the ground state. The rapid changes in Pt-Pt, Tl-Pt and ΔT seen in a 100 fs window around $\Delta t = 0$ is not interpreted as real due to the momentary spike in temperature being unphysical. There is a slight ~ 0.5 ps delay in the grow in of the temperature which matches the behaviour of temporal trace shown in Figure 5.6. That the model predicts an initial Pt-Pt bond elongation is curious since in the case of PtPOP it is the reverse. One possible explanation for this oddity could be that the Tl-Pt and Pt-Pt distance are too correlated to be disentangled. Another possibility is that the inclusion of a cage signal of Tl-PtPOP in the model would affect the outcome of the dynamics. This is, however, deemed unlikely as any cage signal would likely be a small contribution. It would also not be expected to change the dynamics of the model since any cage signal would be a constant contribution for every time delay.

In the next chapter the influence of the cage contribution and correlated parameters on a structural analysis is discussed in light of a high energy TR-WAXS simulation.

Improving structural determination with high energy TR-WAXS 6

A general consensus in the TR-WAXS community is that access to high X-ray energies for TR-WAXS would improve the experiment as higher scattering vectors, Q , can be reached. An argument for this is that the solvent and cage contributions to a ΔS is primarily dominant in the mid range Q ($Q \in [0.5, 5]$) while the solute contribution persists for even large values of Q as shown for the case of PtPOP in Figure 6.1 left hand side.

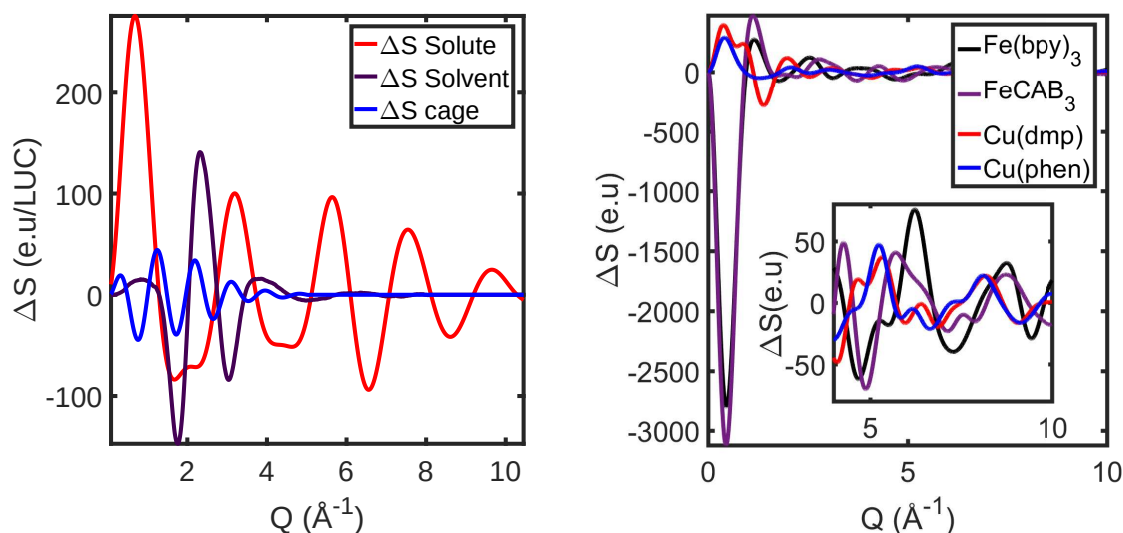


Figure 6.1: Left: The theoretical $\Delta S(Q)$ contributions of a 12 mM aqueous solution of PtPOP; The DFT predicted $\Delta S(Q)$ of PtPOP (red), the solvent $\Delta S(Q)$ from a reference measurement (purple) and the cage contribution predicted from QMMM (blue). Right: The DFT predicted difference scattering signal of the $[\text{Fe}(\text{bpy})_3]^{2+}$ high spin state (black), the $[\text{Fe}(\text{btbip})_2]^{2+}$ quintet state (purple), the $[\text{Cu}(\text{dmp})(\text{POP})][\text{BF}_4]$ lowest triplet state (red) and the $[\text{Cu}(\text{phen})(\text{POP})][\text{BF}_4]$ lowest triplet state (blue).

Another argument is that the amount of structural information that can be obtained from a TR-WAXS study is related the number of independent data points of a TR-WAXS signal. The number of independent data points of a signal is addressed for XAFS in [54]. Based on this study, [22] propose that the number of independent data points, N , in a TR-WAXS signal is given as the Q dependent expression,

$$N = 2\Delta Q D_{max}/\pi \quad (6.1)$$

where ΔQ is the range of scattering vectors (momentum transfers) and D_{max} is the size of the molecular system. However, any advantages that might be gained from the access to higher Q , as opposed TR-WAXS with mid Q ranges, have never been explicitly shown nor has it been discussed in light of data related noise or experimental design parameters.

Synchrotrons as opposed to XFEL's readily provides high energy X-rays but lack the time resolution and the peak brilliance of an XFEL. Access to high energy X-rays in combination with femtosecond time resolution and high peak brilliance is promised with the commissioning of the European X-ray Free Electron Laser. For the Swiss Free Electron Laser and the upgrade of Linac Coherent Light Source (LCLS-II), higher X-ray energies can be reached with higher harmonics though at the price of a reduced X-ray brilliance. Thus with the imminent new XFEL facilities the question of what is gained from high energy TR-WAXS is an increasingly pressing topic.

The focus of this chapter is to elucidate how the structural analysis of TR-WAXS data may benefit from high energy X-rays. The approach to this topic is simulate the scattering data which would otherwise normally be obtained from TR-WAXS experiments. This is done for X-ray energies up to 18 keV and with simulated experimental parameters as close as possible to current XFEL experimental parameters (further elaborated below). This approach is chosen in order to generate data with a noise profile as realistic as possible. A structural analysis is then applied to simulated data and the uncertainties and precision related to this procedure is tracked both as function of the X-ray energy and of the noise level of the simulated data.

6.1 Simulating ground and excited state 2D scattering patterns

In a TR-WAXS experiment the scattered intensity seen by the detector depends on a number of things such as the number of scatters, the number of photons in the X-ray pulse, the solid angle seen by the pixels etc. First and foremost the squared molecular form factor of the scattered system encodes the scattering probability distribution. The squared molecular form factor, $S(Q)$, at a given scattering vector, $Q = 4\pi/\lambda \sin(2\theta/2)$,

is determined by the X-ray energy and the probed molecular structure through the

$$S(Q) = r_0^2 \sum_{i,j}^N f_i^* f_j e^{i\mathbf{Q} \cdot \mathbf{r}_{ij}}, \quad (6.2)$$

where r_0 is the Thomson scattering length, $f_{i,j}$ is the atomic form factor, and r_{ij} is the atomic distance between the i 'th and the j 'th atom. Thus the scattering profile of any system can be calculated provided the that molecular structure is known. Due to its simplicity and familiarity the molecular system of choice is PtPOP in aqueous solution. The starting point of any TR-WAXS structural analysis is the 1d difference scattering signal,

$$\Delta S(Q) = S(Q)_{on} - S(Q)_{off}. \quad (6.3)$$

Thus to simulate the difference scattering signal of PtPOP requires a choice in both the *on* and *off* structural configuration. For this study the *off* scattering is based on the DFT calculated ground state structure of PtPOP while the *on* scattering is based on the triplet excited state structure of PtPOP.

The starting point is to simulate the 2D scattering patterns as would be recorded in a TR-WAXS experiment. For Equation 6.2 to be converted to scattered intensity requires the expression to be multiplied with; the number of photons per X-ray photons per cross sectional area of the X-ray pulse; the number of scatters in the spatial volume (X-ray cross sectional area multiplied with jet thickness) and the solid angle covered by a given pixel. To simulate 2D scattering patterns with a pixel resolution of 1-2 million pixels as would be the case of the CSPAD [24], the LPD [55] or the Pilatus detector [56] is computational heavy task. The scattering patterns are instead simulated 500x500 pixel detector with each pixel covering an area of 440x440 μm . The sample-to-detector distance is chosen as 5 cm allowing for scattering angles up to ≈ 71 degrees to be simulated. The probed sample volume is set by a liquid sheet thickness of 100 μm combined with an X-ray cross section of 100x100 μm . The simulated sample volume contains a 12 mM concentration of PtPOP in aqueous solution and is probed by 10^{12} photons per pattern simulated. The 10^{12} photons per scattering pattern approximately corresponds to the number of photons contained within an X-ray pulse at LCLS and the chosen jet thickness and sample concentration in line with recent XFEL experiments. The total scattering simulated for the detector is the coherent and incoherent sum of the X-ray scattering of the sample,

$$S = S_{Coherent\ Solute} + S_{Incoherent\ Solute} + S_{Coherent\ Solvent} + S_{Incoherent\ Solvent}. \quad (6.4)$$

The *incoherent* scattering of the solvent is calculated while for the *coherent* scattering of the solvent a reference is used [29]. The energy dependent fluorescence has been omitted.

The combination of sample/detector geometry, sample concentration, # photons, molecular form factor and scattering cross section determines the intensity seen by the detector. In turn the intensity determines the associated Poisson noise seen by each pixel in the corresponding detector scattering pattern. The underlying readout noise of each pixel is set to 10^4 photons/pixel and modelled as normal distributed and is centred around zero counts. Centring the noise around zero corresponds having performed a subtraction of the signal contribution arising from the dark current response of the detector. The simulated detector pattern is corrected for solid angle, X-ray polarisation and detector absorption layer efficiency as discussed in Section 3.1.3. The detector absorption efficiency is calculated for each pixel having a silicon absorber layer with a thickness of $500\text{ }\mu\text{m}$ as would be case for the CSPAD detector. The relative magnitude of the three corrections are shown in Figure 6.2.

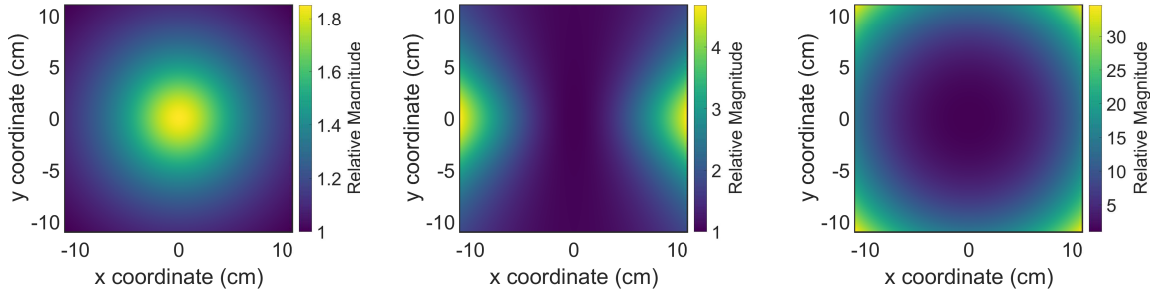


Figure 6.2: The detector corrections applied in the simulation of scattering patterns. Displayed as the relative magnitude for the chosen detector geometry. Left: Detector absorption efficiency. Middle: X-ray polarisation. Right: Solid angle coverage.

The theoretical 2D scattering of the ground state of the aqueous solution of PtPOP is shown in the left hand side of Figure 6.3. On the right hand side of the same figure the radially integrated scattering signal is shown as is the coherent and incoherent contributions constituting the total scattering signal.

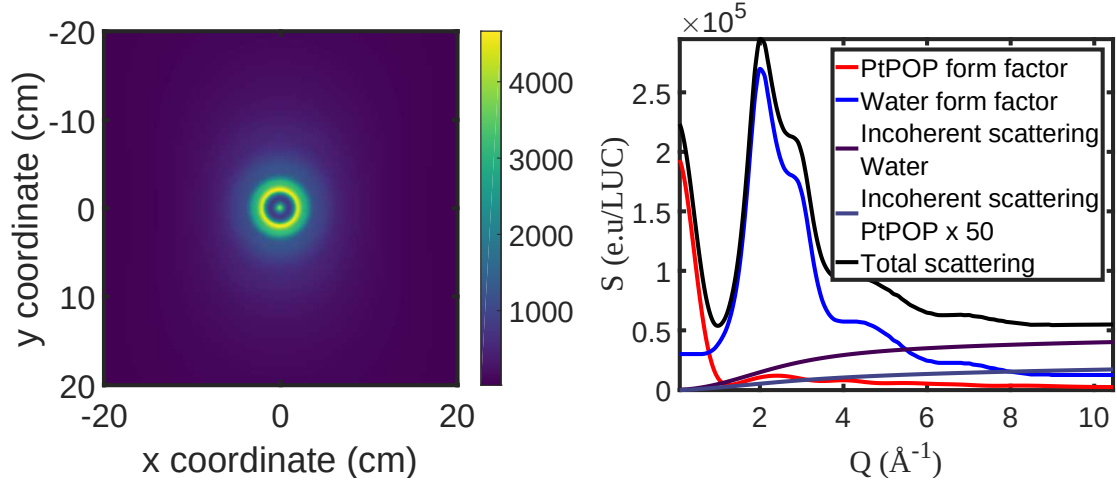


Figure 6.3: The theoretical scattering of a 12 mM aqueous solution of PtPOP. Left: The 2D scattering pattern before applying the detector corrections. The colorbar shows the scattering intensity. Right: The radially integrated coherent and incoherent scattering contributions, of the 2D scattering pattern, given in electron units per liquid unit cell.

Ingrained in the simulated $\Delta S(Q)$ is that the PtPt bond length of PtPOP contracts by 0.2 Å as this corresponds to the structural DFT predictions of the ground state and the triplet excited state. The same order of contraction is from a TR-WAXS study by Morten et al[58]. Furthermore in the $\Delta S(Q)$ the excitation fraction, α , and the temperature increase, ΔT , is chosen as 20 % and 0.4 K respectively and have magnitudes commonly found in TR-WAXS studies. The theoretical contributions of the $\Delta S(Q)$ is shown in Figure 6.1 left hand side.

The $\Delta S(Q)$ signals are calculated for X-ray energies from 6-18 keV in steps of 0.5 keV. For each X-ray energy a 1000 2D scattering patterns are simulated for the ground state and the excited state. From these the resultant 1000 2D difference patterns are azimuthally integrated giving for each energy a total of 1000 1D $\Delta S(Q)$. Left-hand side and middle of Figure 6.4 shows the averaged $\Delta S(Q)$ curves for 6 and 18 keV respectively. On the right-hand side of Figure 6.4 the progression of corresponding mean noise, $\langle \sigma(Q) \rangle$, of the $\Delta S(Q)$ of 6 keV and 18 keV is shown for the progressively averaged ΔS scattering curves.

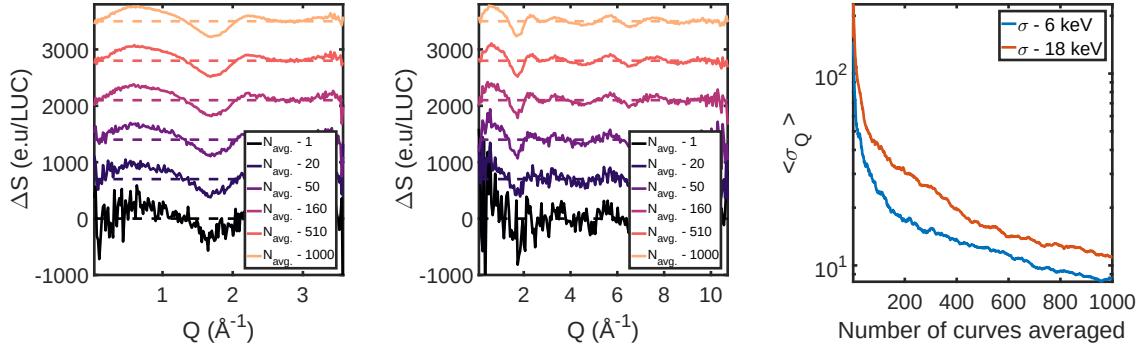


Figure 6.4: Radially integrated simulated $\Delta S(Q)$ scattering curves and the associated noise shown for the average of N $\Delta S(Q)$ curves. Left: Simulated scattering curves of 6 keV. Middle: Simulated scattering curves of 18 keV. Right: The average noise, $\langle \sigma_Q \rangle$, of the averaged $\Delta S(Q)$ curves compared for 6 and 18 keV.

Having simulated multiple 1D $\Delta S(Q)$ curves the structural analysis of these curves can be examined both as a function of the Q space coverage and the number of curves averaged. The latter is of interest as the noise of a given $\Delta S(Q)$ curve decreases with the number of curves averaged. The question remains of what model to use in the structural analysis of the simulated difference signals. As the data is simulated the exact/complete model needed to describe the data is known. But modelling the simulated data with a perfect model should not be dependent on the Q -space coverage but should describe the data equally well for all Q scattering vectors. Rather what is interesting is to model the data with an incomplete model and see how prediction power of an incomplete model changes as the Q -space coverage changes.

In some of the early TR-WAXS studies the cage signal was omitted in the structural analysis as the framework to properly describe it was not thoroughly developed. Since then the framework for calculating the cage signal has improved but nonetheless calculating the cage signal is not always straight forward as different DFT force fields yields different results in the description of the cage signal. Calculating the cage can also be a computational heavy process as in the case of using quantum mechanic molecular modelling to calculate it. Thus a incomplete model candidate would be model in which the contribution from the cage signal is omitted. The structural analysis of the simulated $\Delta S(Q)$ using a complete and incomplete model is further elaborated in the next section.

6.2 Quantitative interpretation of the simulated data

The simulated 1D $\Delta S(Q)$ is averaged over the 1000 simulated $\Delta S(Q)$ curves and compared to a complete and incomplete model. The purpose of comparing a

complete and an incomplete model is to investigate if the additional Q-space coverage, acquired for larger E_{max}^{X-ray} , provides sufficient additional information for the better determination of the simulated parameters despite the model being incomplete. The incomplete model miss the structural contribution from the solvent cage and is only modelled as the combined difference scattering of the solute and the solvent. The missing cage contribution for the incomplete model is primarily dominant in the low Q region ($Q \in [0,5]$). Thus as the Q-space coverage increases the missing cage contribution is weighted less compared to the weight of the solute contribution which is significant for the entire Q-space range. The complete model is complete in the sense that the three structural contributions with which the TR-WAXS data is simulated is used in the complete model. A complete models ability to correctly describe data should be independent of the X-ray energy and thus the complete model serves as a reference frame. The complete model, ΔS_{CM} , consists of a parametrization of the tree structural terms of which the difference signals are simulated. The solute term represents the structural changes of the solute. For the specific case of PtPOP the primary structural change is the PtPt distance. The solvent term arises from the change in the pair correlation function of the solvent due to heating. The solvent-solute cross (or cage) term represents the solvent molecules in proximity of the solute structurally differ from the bulk solvent due to solute-induced solvent rearrangement. The complete model, ΔS_{CM} , is expressed as:

$$\Delta S_{CM} = \alpha \cdot (\Delta S_{sol}(PtPt) + \Delta S_{cage}) + \Delta T \left. \frac{\partial S_{H_2O}}{\partial T} \right|_{\rho}, \quad (6.5)$$

while for the incomplete model ΔS_{INCM} the cage term is omitted,

$$\Delta S_{INCM} = \alpha \cdot \Delta S_{sol}(PtPt) + \Delta T \left. \frac{\partial S_{H_2O}}{\partial T} \right|_{\rho}. \quad (6.6)$$

In Equations (6.5) and (6.6) α is the excited state fraction of the solute and ΔT is the temperature increase of the solvent. The $PtPt$ of the solute term refers to the parametrization of the PtPt distance of the excited state of the solute. The excited state fraction, α , the temperature increase, ΔT and the $PtPt$ distance of the solute are free parameters within the limits of a predefined grid-based parameter space. The grid has the dimensions 91x161x500 and confines α in the range of 0-100%, ΔT in the range 0-0.8 K and the PtPt distance of the excited state in the range 1.768 - 3.768 Å. Each point of the grid thus gives rise to a unique model. For each model a χ^2 value is assigned when compared to a $\Delta S(Q)$ using Equation 2.10. The resultant 3D χ^2 solution space is subsequently converted to likelihood space through the relation,

$$L(P1, ..., P_m) \propto e^{\frac{-\chi^2}{2}}, \quad (6.7)$$

where L is the likelihood for the parameter set of $P1, ..., P_m$. The 1,2,3- σ are the confidence intervals corresponding to 68.28%, 95.45% and 99.73% [57, 59]. The hypersurfaces defined by 1,2,3- σ contours of the 3D maximum likelihood space is

projected onto the parametrization-surfaces which gives the 2D likelihood maps. These hypersurfaces have three projections. These three projections are shown in Figure 6.5 as obtained from the 9 keV structural analysis.

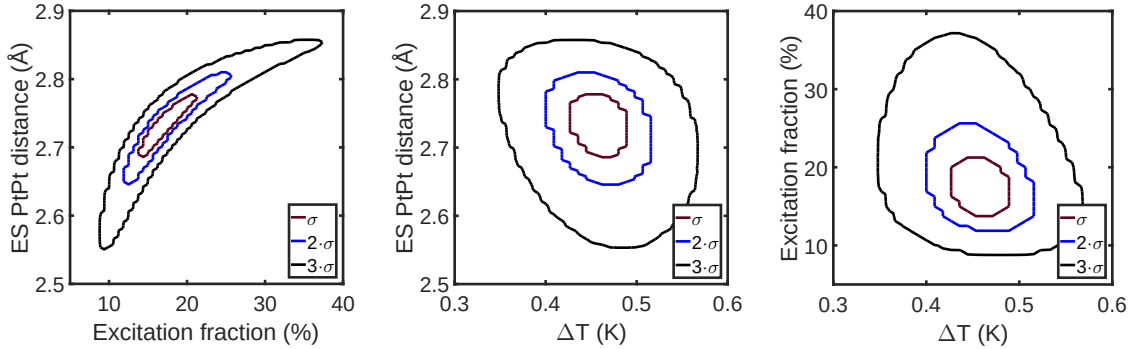


Figure 6.5: The correlation maps as found from the projection of the 1,2,3- σ confined hypersurfaces of the 3D maximum likelihood space. Shown for the 3D maximum likelihood space associated to the χ^2 structural analysis of the 9 keV simulated $\Delta S(Q)$. Left: The correlation map spanned by the excited state Pt-Pt bond length and the excitation fraction. Middle: The correlation map spanned by the excited state Pt-Pt bond length and the temperature increase. Right: The correlation map spanned by the excitation fraction and the temperature increase.

The three projections represent: The correlation between the PtPt distance and the excitation fraction shown on the left hand side of the figure; The correlation between PtPt distance and the temperature increase, shown in the middle of the figure, and the correlation between the excitation fraction and the temperature increase, shown on the right hand side of the figure.

The 2D likelihood correlation maps are projected onto their respective parameter axes and from these the full width of the projection is the uncertainty of the maximum likelihood value of a given parameter.

6.3 Correlation between parameters

As can be seen qualitatively from Figure 6.5 some degree of correlation between the parameters exist. A consequence of correlated parameters is that the true value of each parameter is less certain. Strong correlations are thus problematic as it may lead to two widely different structural solutions being equally likely. The challenge of simultaneous determination of a set of parameters is encoded in the parameters correlation factor. The correlation factor may be extracted from the 2D correlation maps by computing the Pearson linear correlation factor,

$$r = \frac{\sum_i (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_i (x_i - \bar{x})^2} \sqrt{\sum_i (y_i - \bar{y})^2}} \quad [59], \quad (6.8)$$

where (x_i, y_i) are the pairs of points contained within 1σ contour of a given 2D correlation map. The r , as calculated for the pairs of points contained within 1σ of the three 2D correlation maps is 0.8544, -0.1041 and -0.0462 respectively. Values of r close to zero indicate that the correlation is small while values close to 1 or -1 represents strong correlation or anti-correlation. A significant correlation primarily exist between the excited state PtPt distance and the excitation fraction. Figure 6.6 shows the r values for the three correlation parameters as a function of the X-ray energy.

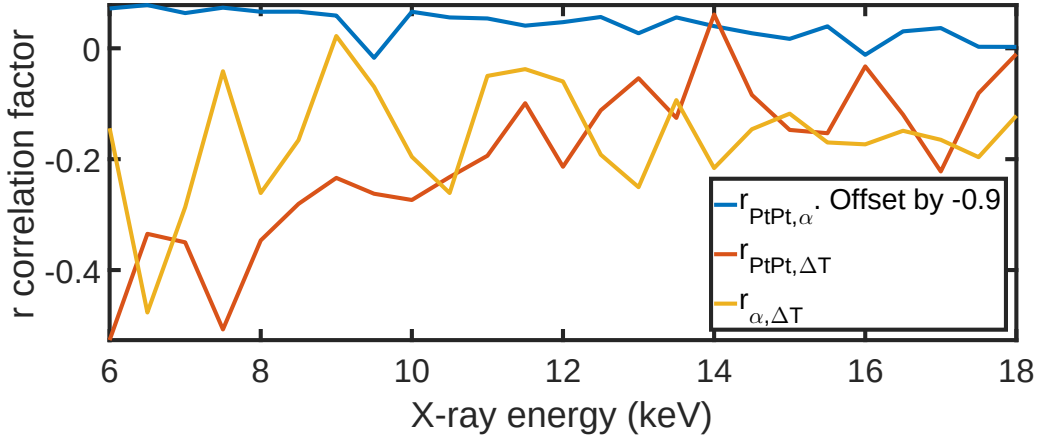


Figure 6.6: The Pearson correlation factor, r , as calculated for the pairs of points contained within 1σ of the 2D correlation maps. Calculated for the 2D correlation maps associated with the X-ray energies ranging from 6 to 18 keV. The correlation between the Pt-Pt bond length and the excitation fraction (blue curve), the correlation between the Pt-Pt bond length and the temperature increase (red curve) and the correlation between the excitation fraction and the temperature increase (orange curve).

From the figure it is seen that the strength of the correlations decrease with the access to higher energies. However, a strong correlation between the PtPt distance and α remain persists.

6.4 Best fit model parameters

In addition to the r value of the 2D correlation maps, other key values which can be extracted from the correlation maps are the minimum χ^2 and the associated best fit parameter values. Figure 6.7 shows the simulated $\Delta S(Q)$ and the best fit model for the X-ray energies of 6, 12 and 18 keV. The middle of the figure shows the χ^2 value of the best fit as given for the complete and incomplete model for the entire X-ray energy range. The right hand side of the figure shows the residual found from subtracting the best fit model from the simulated data. The residuals are overlaid with the cage model component to demonstrate how the residual represents the missing cage for high X-ray energies.

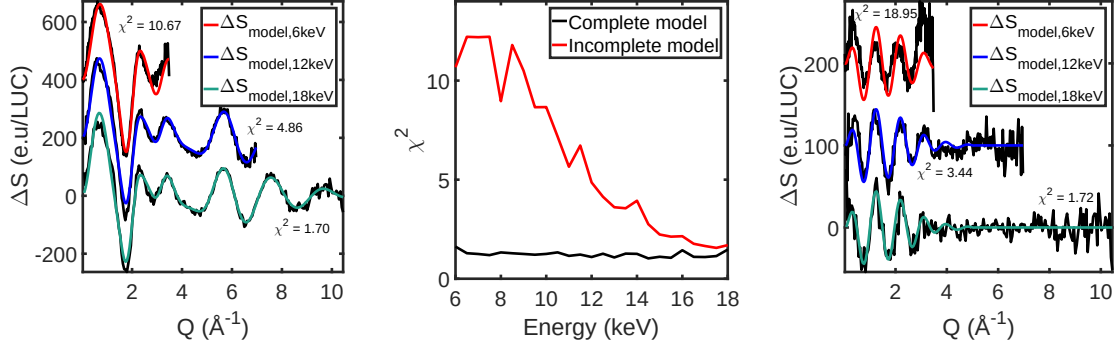


Figure 6.7: Left: The simulated $\Delta S(Q)$ (black curve) averaged for 1000 curves compared for 6, 12 and 18 keV. The simulated data is offset by 200 and overlaid with the (incomplete) best fit solution obtained from the χ^2 analysis. The χ^2 value of the solution are shown as an inset. Middle: The χ^2 values of the complete and incomplete best fit models shown for X-ray energies ranging from 6 to 18 keV. Right: The residual (black curve) between the simulated $\Delta S(Q)$ averaged for 1000 curves and the best fit solution. The simulated data is offset by 100 and overlaid with the "missing" cage model component. The χ^2 values of the cage model component, as compared to the residuals, are shown as an inset.

As the Q -space coverage is extended the χ^2 values of the best fit model improves for the incomplete model while the χ^2 of the complete model is largely unaffected. The energy evolution of the best fit parametric values of the complete and incomplete model are shown in Figure 6.8.

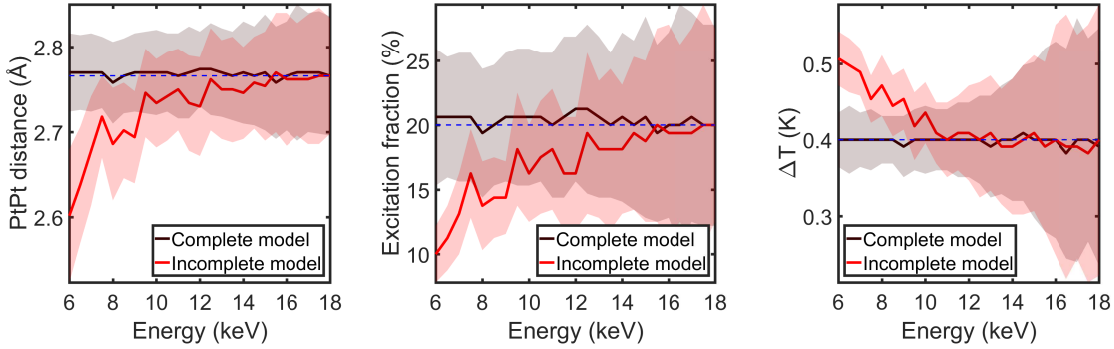


Figure 6.8: The parametric values of the best fit solutions obtained from the χ^2 analysis, shown for both the complete and incomplete model, for X-ray energies ranging from 6 to 18 keV. The shaded area of a given curve shows the associated 1σ uncertainty. The blue dashed line indicates the parameter value with which the $\Delta S(Q)$ is simulated. Left: The excited state Pt-Pt distance. Middle: The excitation fraction Right: The temperature increase, ΔT .

From the figure two important trends are seen. First, the incomplete models ability to correctly predict the parameter values of the simulation is improved as the X-ray

energy increases. Secondly, the increase in parameter precision comes at the price of a decrease in the certainty. This is related to the noise of each Q-bin which changes as the X-ray energy changes. As the X-ray energy increases the noise of the low Q region also increases. This is because the majority of the pixels of the detector is moved towards larger Q-scattering vectors as the X-ray energy increases. To illustrate this the pixel count for each Q scattering vector is shown in Figure 6.9 for multiple X-ray energies.

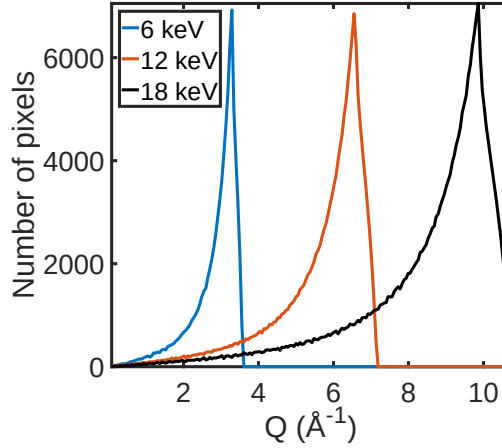


Figure 6.9: The number of pixels found for each scattering vector Q when dividing the Q range into 200 bins. Shown for the X-ray energies of 6, 12 and 18 keV.

As the solute contribution is dominant for the entire Q -range the uncertainty of this parameter does not suffer to the same extend as uncertainty of the α and ΔT parameters.

6.5 The effect of noise in a structural analysis

The structural analysis presented in the previous section used $\Delta S(Q)$ signals averaged over a 1000 simulated signals. Needless to say the structural analysis could have been performed for $\Delta S(Q)$ averaged over any number of curves (though limited by the number of curves simulated). Performing the same structural analysis of the $\Delta S(Q)$ as it is progressively averaged over additional curves, may help illuminate how noise effects the structural analysis. For each combination of X-ray energy and number of curves averaged, the parametric values of best fit solution and the associated 1σ uncertainties are extracted and shown as 2D colormaps in Figures 6.10, 6.11 and 6.12.

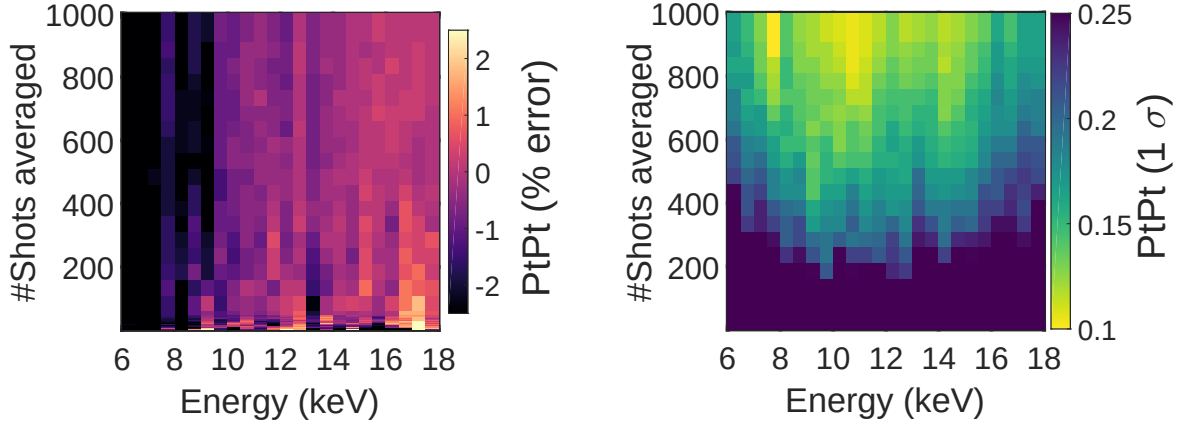


Figure 6.10: Left: The excited state Pt-Pt parametric values of the best fit solutions obtained from the χ^2 analysis of the incomplete model for X-ray energies ranging from 6 to 18 keV and the number of curves averaged ranging from 1 to 1000. Right: The 1 σ uncertainty of the excited state PtPt distance.

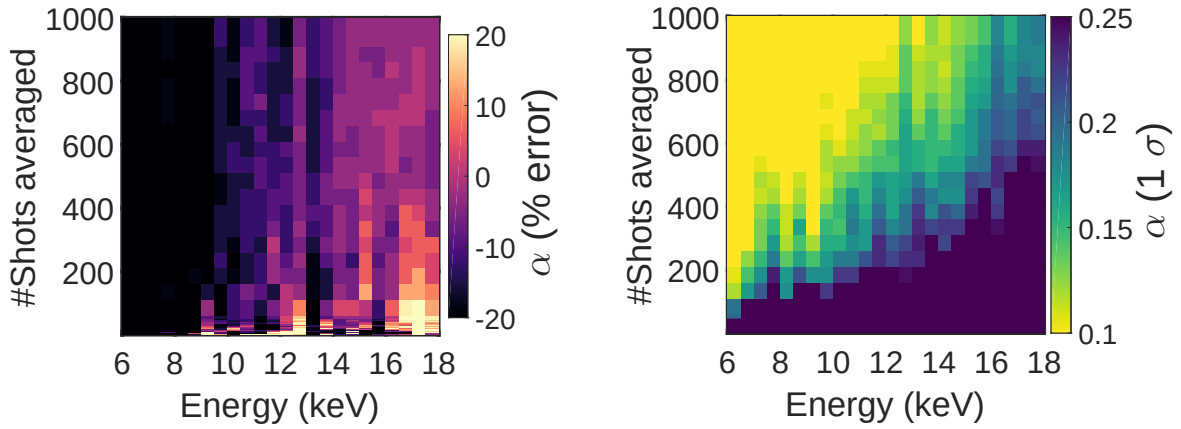


Figure 6.11: Left: The excitation fraction parametric values of the best fit solutions obtained from the χ^2 analysis of the incomplete model for X-ray energies ranging from 6 to 18 keV and the number of curves averaged ranging from 1 to 1000. Right: The 1 σ uncertainty of the excitation fraction.

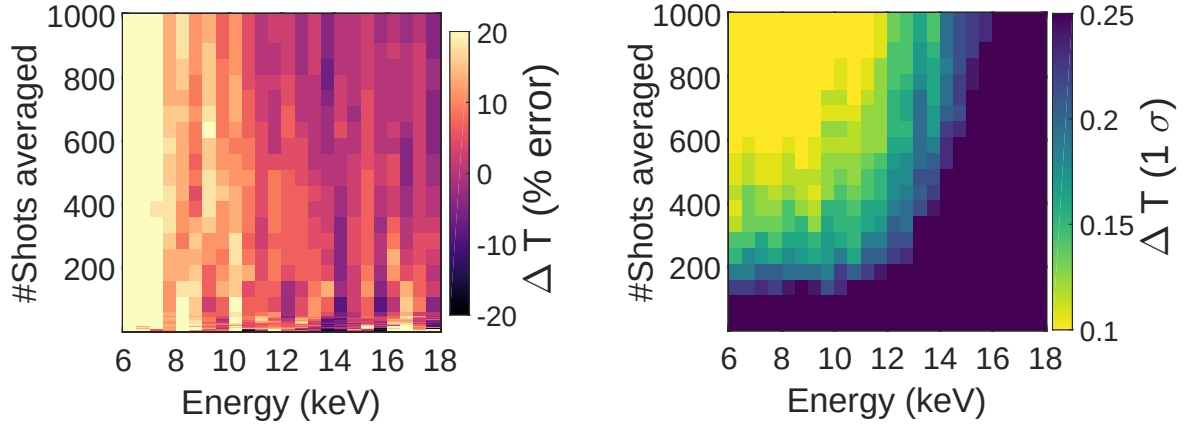


Figure 6.12: The temperature increase parametric values of the best fit solutions obtained from the χ^2 analysis of the incomplete model for X-ray energies ranging from 6 to 18 keV and the number of curves averaged ranging from 1 to 1000. Right: The 1σ uncertainty of the temperature increase.

From figures 6.10, 6.11 and 6.12 it is seen that averaging decreases the 1σ uncertainty. However, it does not qualitatively improve the ability to determine the correct model parameters. This is perhaps not surprising as the 1σ uncertainty does not reflect the likelihood of a given model. Rather, how the structural analysis benefits the averaging is seen in the χ^2 map shown in Figure 6.13.

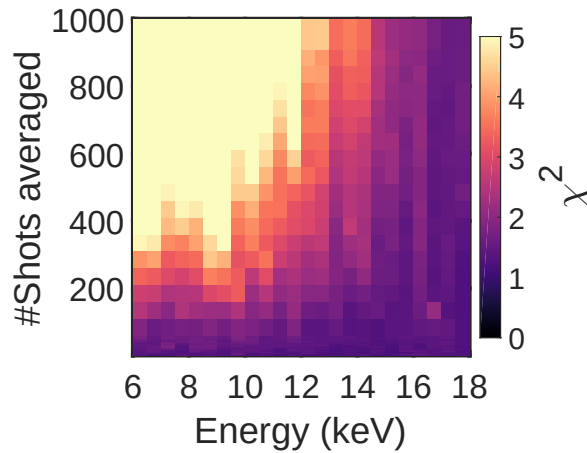


Figure 6.13: The χ^2 value of the best fit solutions obtained from the χ^2 analysis of the incomplete model for X-ray energies ranging from 6 to 18 keV and the number of curves averaged ranging from 1 to 1000.

As can be seen from the figure, the χ^2 value is larger for an incorrect model. Thus low noise signals (more averaging) is the determining factor in deducing the validity

of a given model while the Q-space coverage is the dominant factor in determining a correct model.

6.6 Summary and discussion

A TR-WAXS experiment has been simulated for X-ray energies ranging from 6 to 18 keV. Specifically the X-ray scattering of the ground and excited state of PtPOP was simulated and used to construct difference scattering signals. For each X-ray energy the difference scattering signals were compared to a set of parametrized complete and an incomplete models in a χ^2 framework and the parametric values of the model fits were tracked as a function of both the X-ray energy and the number of difference curves averaged. The purpose of this was elucidate to what extend a TR-WAXS study benefits from the access of high energy X-rays. Tracking the parametric values associated with the minimum χ^2 values allowed for the determination of the prediction power of the complete and incomplete model. The complete model served as a reference and did, unsurprisingly, not benefit from higher X-ray energies. However, as seen from Figure 6.8 the incomplete models ability to correctly predict the parametric values is dependent on the X-ray energy, with higher X-ray energies enabling a more precise result though at a price of an increased uncertainty. The increased uncertainty is believed to be related to the pixel count for each Q value and may be improved with additional averaging of curves. As opposed to the complete model, the incomplete model did include a cage contribution, a choice made as this has also been the case for several experimental TR-WAXS studies. The incomplete models ability to correctly predict the parametric values when using high energy X-rays enables the extraction of the true solvent cage signal as seen in the right hand side of Figure 6.7. Thus, with the access to higher X-ray energies a TR-WAXS experiment has the opportunity to provide direct feedback of the cage signal to computational chemists.

Summary and Conclusion

This thesis describes and demonstrates how X-ray scattering can be used for the study of the ultrafast photochemical processes of transition metal complexes in solution. In Chapter 2, the theoretical foundation of X-ray scattering was presented, as were the governing principles of an XFEL. Furthermore, it was outlined how X-ray scattering is used in TR-WAXS at XFEL's to study the ultrafast photophysics of transition metal complexes in solution on the femtosecond time scale. In Chapter 3, the data reduction and treatment process of TR-WAXS XFEL data was described. This process was used to reduce the TR-WAXS experimental data presented in [IV,VIII,X].

Chapter 4 presented the results of an XFEL study [IV] on the photo-fragmentation life cycle of $(\text{Ru}_3\text{CO}_{12})$. The first 50 ps following the photo-excitation of $(\text{Ru}_3\text{CO}_{12})$ in cyclohexane was studied using TR-WAXS with 100-femtosecond time resolution. From our analysis of the experimental data we found that three intermediates are formed, successively, in the first 50 ps of the photo-fragmentation life cycle. We propose that at the onset of the reaction the absorption of 400 nm photon leads to Ru-Ru bond breakage and the formation of the carbonyl bridged structure, $\text{Ru}_3(\text{CO})_{11}(\mu-\text{CO})$. This is the dominant species in the first 1.5 ps. After 1.5 ps our analysis suggest the formation of a previously not reported triple CO bridged intermediate, $\text{Ru}_3(\text{CO})_8(\mu-\text{CO})_3$ which lives for ~ 9 ps. The third and last intermediate suggested by our analysis is $\text{Ru}_3(\text{CO})_{10}$. This intermediate is the dominant species at the latest time point in our data, 50 ps. The same intermediate was suggested from synchrotron based TR-WAXS studies of $\text{Ru}_3\text{CO}_{12}$. This connects our sub 50 ps results with the post 50 ps results from synchrotron based studies in the literature. The first intermediate, $\text{Ru}_3(\text{CO})_{11}(\mu-\text{CO})$, is suggested in the literature from complementary optical techniques. Thus our proposal for the photo-fragmentation cycle of $\text{Ru}_3(\text{CO})_{12}$ is consistent with earlier optical and synchrotron based TR-WAXS studies of the system. We speculate that the suggested new intermediate could have escaped detection of earlier optical studies, due to the IR-signatures of the single bridged and triple bridged structures having overlapping features and making them difficult to discern.

Chapter 5 presented our results of a (2015) XFEL study [VIII] on the ultrafast (>5 ps) dynamics of Tl-PtPOP. The first 5 ps of the system following photo-excitation was studied using optical TA and TR-WAXS. The oscillatory structural signal of the experimental data was isolated and subjected to a Time-domain Fourier transform. The

Fourier transform of TA and TR-WAXS revealed two dominant modes, ~ 230 fs and ~ 290 fs. Similar modes of PtPOP have been reported in the literature and ascribed to the excited state and ground state Pt-Pt vibration of PtPOP. The time domain Fourier transform of TR-WAXS data of PtPOP in solution only show the presence of the ~ 290 fs mode following photo-excitation at 395 nm. However, time domain Fourier transform of TR-WAXS data of Tl-PtPOP in solution show the presence of both the ~ 230 fs and ~ 290 fs mode. This was interpreted as the aqueous solution of Tl-PtPOP containing both Tl-PtPOP and PtPOP. No ground state structure of Tl-PtPOP is available from the literature. Instead the ground state structure of Tl-PtPOP was estimated through the structural optimization of the 5 ps difference signal. From our analysis we suggest a Pt-Pt distance of ~ 2.94 Å and a Tl-Pt distance of ~ 3.44 Å. This Pt-Pt distance of Tl-PtPOP is comparable to the ~ 2.9 - 3.0 Å Pt-Pt distance reported for PtPOP. The Tl-Pt distance is ~ 0.5 Å longer than in the excited state. This relatively large difference in distance between the ground and excited state is assigned to the weak association of Tl to PtPOP in the ground state. The estimated ground state structure was used to uncover the structural dynamics of Tl-PtPOP in the first 5 ps after photo-excitation. Following photo-excitation of Tl-PtPOP in aqueous solution we find an initial elongation of the Pt-Pt distance followed by a contraction while the Tl-Pt distance contracts. This result is somewhat puzzling as for the case of PtPOP the Pt-Pt distance contracts.

Chapter 6 presented the results of a study of the potential role of utilizing high energy X-rays in the structural analysis of TR-WAXS. TR-WAXS data of PtPOP in aqueous solution was simulated for X-ray energies between 6 and 18 keV. Difference signals were constructed from simulated structures and modelled using a complete and an incomplete model. Given a complete model it was shown that a TR-WAXS structural analysis does not benefit from the access to higher X-ray energies. The incomplete model was constructed without a component for the cage. To mimic some of the early TR-WAXS studies in the literature in which the structural analysis did not include a cage response. The missing cage contribution in the incomplete model resulted in the model predicting a different structure of PtPOP for each the X-ray energy. It was shown that the error in the predicted PtPOP structure was progressively lessened when increasing the Q-space coverage of the TR-WAXS data. The better estimates of the structure of PtPOP is interpreted as connected to the cage component only being dominant in the Q mid range while the solute contribution is dominant in the entire Q range. Furthermore, it was shown that as the X-ray energy increases, the residual between simulated data and best fit model resemble the missing cage contribution. Thus, it is concluded that the access to higher X-ray energies in a TR-WAXS experiment provides the opportunity to grant direct feedback of the cage contribution to computational chemists.

Outlook

In Chapter 5, a potential error in the model of Tl-PtPOP was that the model did not include a contribution from the solute-solvent cage of TlPtPOP. A calculation of the solute-solvent cage was not possible due to the ground state structure of Tl-PtPOP being unknown. Thus, with the new estimate for the ground state structure the cage contribution could be estimated from molecular modelling. As seen in Chapter 6 a missing cage contribution will likely effect the parametric values of a best fit solution. How much the parametric values are effected should be connected to how large the cage contribution is in relation to the solute and solvent contributions. It would therefore be of interest to calculate the cage of Tl-PtPOP and see how it effects the structural dynamics.

With the recent commissioning of the European XFEL it will soon be possible to perform a high energy TR-WAXS experiment. While it has been possible to reach high energy X-rays (~ 21 keV) at LCLS using higher harmonics, it comes at a price of a decreased intensity of the X-ray pulses by a factor of ~ 10 . The decreased intensity, in turn, decreases the signal to noise ratio and requires the averaging of more data. This issue is solved by Mhz rep rate of the European XFEL which will, when fully operational, provide $\sim 10^4$ more X-ray pulses compared to LCLS and SACLA XFEL's. Using the combination of high X-ray energy and the Mhz rep rate of the European XFEL it would be interesting to design an experiment for the study of solvent-cage. Such an experiment would highly benefit from high energy X-rays to disentangle contributions from solute, solvent and the cage.

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Papers

Paper I

Tracking the picosecond deactivation dynamics of a photoexcited iron carbene complex by timeresolved X-ray scattering.

Denis Leshchev, Tobias C. B. Harlang, Lisa A. Fredin, Dmitry Khakhulin, Yizhu Liu, Elisa Biasin, **Mads G. Laursen**, Gemma E. Newby, Kristoffer Haldrup, Martin M. Nielsen, Kenneth Warnmark, Villy Sundstrom, Petter Persson, Kasper S. Kjær and Michael Wulff.

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Tracking the picosecond deactivation dynamics of a photoexcited iron carbene complex by time-resolved X-ray scattering†

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Recent years have seen the development of new iron-centered N-heterocyclic carbene (NHC) complexes for solar energy applications. Compared to typical ligand systems, the NHC ligands provide Fe complexes with longer-lived metal-to-ligand charge transfer (MLCT) states. This increased lifetime is ascribed to strong ligand field splitting provided by the NHC ligands that raises the energy levels of the metal centered (MC) states and therefore reduces the deactivation efficiency of MLCT states. Among currently known NHC systems, $[\text{Fe}(\text{btbip})_2]^{2+}$ (btbip = 2,6-bis(3-*tert*-butyl-imidazol-1-ylidene)pyridine) is a unique complex as it exhibits a short-lived MC state with a lifetime on the scale of a few hundreds of picoseconds. Hence, this complex allows for a detailed investigation, using 100 ps X-ray pulses from a synchrotron, of strong ligand field effects on the intermediate MC state in an NHC complex. Here, we use time-resolved wide angle X-ray scattering (TRWAXS) aided by density functional theory (DFT) to investigate the molecular structure, energetics and lifetime of the high-energy MC state in the Fe–NHC complex $[\text{Fe}(\text{btbip})_2]^{2+}$ after excitation to the MLCT manifold. We identify it as a 260 ps metal-centered quintet (^5MC) state, and we refine the molecular structure of the excited-state complex verifying the DFT results. Using information about the hydrodynamic state of the solvent, we also determine, for the first time, the energy of the ^5MC state as 0.75 ± 0.15 eV. Our results demonstrate that due to the increased ligand field strength caused by NHC ligands, upon transition from the ground state to the ^5MC state, the metal to ligand bonds extend by unusually large values: by 0.29 Å in the axial and 0.21 Å in the equatorial direction. These results imply that the transition in the photochemical properties from typical Fe complexes to novel NHC compounds is manifested not only in the destabilization of the MC states, but also in structural distortion of these states.

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Introduction

The development of iron-based photofunctional complexes can provide a cost effective and environmentally benign path towards large-scale solar energy applications. A central challenge in developing light harvesting complexes with 3d

transition metals is their weak ligand field splitting (LFS) compared to their 4d or 5d counterparts. Due to the weak LFS of 3d transition metal complexes, their photoactive metal-to-ligand charge-transfer (MLCT) excited states are efficiently deactivated by lower energy metal-centered high-spin (MC) states. For example, the MLCT states of a prototypical Fe^{II} polypyridyl complex relax to a quintet metal centered (^5MC) state on the hundred femtosecond time scale,^{1–13} whereas the MLCT lifetime of their Ru^{II} polypyridyl analogs are measured in hundreds of nanoseconds.¹⁴ Efforts in understanding and controlling the photocycle of Fe^{II} complexes have spurred intensive studies of ultrafast MLCT $\rightarrow$ ^5MC deactivation, known as light induced spin crossover (SCO).^{1–13,15} Additionally, the SCO phenomenon could potentially be used in novel memory devices,^{16–21} which have prompted studies of the properties of the ^5MC state and recovery to the singlet ground state (GS).^{22–40} In spite of the inherent challenges in utilizing Fe photosensitizers, recent developments of Fe complexes based on

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N-heterocyclic carbene⁴¹ (NHC) and CN^- ligands⁴² have provided MLCT lifetimes on the order of tens of picoseconds. These systems have been developed towards efficient electron injection into TiO_2 electrodes,⁴³ and they have been extended towards photoluminescence in the Fe^{III} oxidation state.⁴⁴ Density functional theory (DFT) calculations have shown that the improved performance of the Fe–NHC systems is due to increased electron density on the metal provided by strong σ -donating NHC ligands which effectively destabilize the unwanted MC states.^{45,46} This results in inhibiting the MLCT deactivation and bypassing the ^5MC state in the excite state cascade similarly to chemically akin Ru^{II} based sensitizers.^{45,46} A different chemical approach was recently introduced with highly strained halogenated polypyridyls which utilize the quintet GS.^{47,48} Here, the structural restrictions from the halogen atoms placed on the ligand side groups increase the energy of the ^3MC state, as well as the crossing barrier between the MLCT and ^3MC states, which results in MLCT lifetimes as long as 17.4 ps.⁴⁸ The rich photophysics of all these novel systems, compared to the traditional polypyridyl-based Fe^{II} SCO complexes, calls for a better understanding how different electronic and structural factors affect the MLCT deactivation cascade. Specifically, a thorough examination of the excited state potential surfaces, *i.e.* characterization of molecular geometries and energies in the various states with both theory and experiments, will help to find the connection between structure and function in these systems. Such mechanistic understanding of their photocycles will help to develop improved synthetic rules for making better photosensitizers for light harvesting applications.

In this work we investigate the structural dynamics of the Fe–NHC complex $[\text{Fe}(\text{btbip})_2]^{2+}$ (btbip = 2,6-bis(3-*tert*-butylimidazol-1-ylidene)pyridine) (Fig. 1) in acetonitrile (MeCN) solution following photo-excitation to the MLCT manifold, in order to examine the impact of the strong NHC ligand field on the excited state structure, energy and relaxation kinetics. The transient optical absorption spectroscopy experiments previously conducted on this complex,⁴⁹ indicated that upon

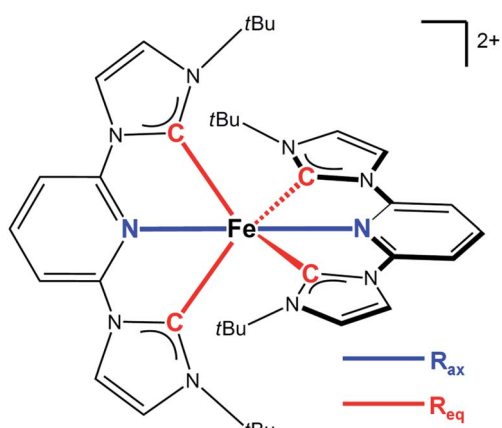
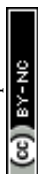


Fig. 1 Structure of the $[\text{Fe}(\text{btbip})_2]^{2+}$ complex studied in this work. The key structural parameters defining the structure of the molecule are highlighted with colors.

excitation to the MLCT manifold, the system decays into a vibrationally hot MC state in 300 fs. A 31 ps component was tentatively assigned to vibrational cooling of this MC state. Complete recovery of the GS spectrum was observed in 230 ps and assigned to GS recovery from the MC state. Since the same compound with methyl (Me) side groups returned to the ground state much faster (~ 10 ps),⁴⁹ the origin of the 230 ps-lived MC state in $[\text{Fe}(\text{btbip})_2]^{2+}$ was ascribed to the presence of the bulky *t*Bu side groups that diminish the LFS of the NHC ligands through steric repulsion. The nature of the excited MC state was initially assigned as a ^5MC state by simple analogy with typical Fe^{II} SCO complexes characterized by weak LFS. Ultrafast MLCT deactivation towards a ^5MC state has also been discussed for $[\text{Fe}(\text{btbip})_2]^{2+}$ based on recent advanced quantum dynamics simulations.⁵⁰ The focus of the work, however, was mainly on the early few-ps dynamics of the relaxation from the initially populated $^1\text{MLCT}$ state rather than on the relaxed intermediate structure associated with the ~ 230 ps excited state lifetime.⁵⁰ On the other hand, the assignment of the intermediate MC state in $[\text{Fe}(\text{btbip})_2]^{2+}$ as ^5MC is in stark contrast with other Fe NHC complexes. For all other Fe NHC complexes, it has been argued that the NHC σ -donation is sufficiently strong to alter the MLCT deactivation pathway to proceed *via* an intermediate ^3MC state, bypassing the ^5MC state altogether.^{41,51–53} Further questions regarding the quintet assignment of the MC state of $[\text{Fe}(\text{btbip})_2]^{2+}$ can be raised based on the recent spectroscopic works on Fe^{II} complexes with expanded cage and push-pull ligands.^{54,55} There, the few-100's ps lifetime of an MC state was suggested to be indicative of its ^3MC character.^{54,55} In line with this suggestion, a 450 ps lived ^3MC state was recently reported for sterically strained Ru^{II} complex with weak LFS.^{56–58} Thus, the 230 ps-lived intermediate MC state of $[\text{Fe}(\text{btbip})_2]^{2+}$ provides a non-trivial case to investigate the competition between strong σ -donation from NHC ligands and steric repulsion caused by *t*Bu groups. On the one hand, $[\text{Fe}(\text{btbip})_2]^{2+}$ is fundamentally different from traditional photosensitizer complexes with long MLCT lifetimes followed by deactivation *via* short-lived ^3MC scavenger states, to which several of the new Fe NHC complexes seem to belong. On the other hand, $[\text{Fe}(\text{btbip})_2]^{2+}$ substantially differs from weak LFS Fe^{II} SCO complexes that deactivate to metastable ^5MC states, often with ns or longer lifetimes. Therefore, determining the spin, structure and energy of the intermediate MC state in $[\text{Fe}(\text{btbip})_2]^{2+}$ will provides new insight in the deactivation cascade of novel Fe^{II} complexes.

Recent progress in time-resolved X-ray methods provides timely opportunities to characterize the photophysics of $[\text{Fe}(\text{btbip})_2]^{2+}$ in greater detail.^{25,59–63} In this work we employ time-resolved wide angle X-ray scattering (TRWAXS) – an established technique which probes the structural changes in the solute with sub-Å precision,^{25,59} making it suitable for monitoring the character and structure of the excited MC state in $[\text{Fe}(\text{btbip})_2]^{2+}$. Since the lifetime of the intermediate MC state in $[\text{Fe}(\text{btbip})_2]^{2+}$ is on the order of hundreds of picoseconds, the properties of this state can be firmly characterized by a synchrotron-based time-resolved experiment taking advantage of the high stability and energy tunability of the X-ray source. The latter provides an opportunity of using high



energy X-rays allowing the measurement of scattering patterns up to high scattering vectors $q \geq 10 \text{ \AA}^{-1}$, a great advantage for the refinement of the excited state structures. TRWAXS is also highly sensitive to the time dependent thermodynamic response of the solvent,⁵⁹ which, as we demonstrate in this work, can be used to determine the energy of the excited states. In parallel with the TRWAXS measurements, we perform extensive DFT calculations to support the experimental findings regarding the structure and energy. By comparing the DFT results obtained using different functionals with the experimental data, we identify the ones providing the best agreement with the data in order to improve future theoretical predictions. This detailed combination of computational and experimental characterization deepens our understanding of the NHC family of compounds.

Experimental

The TRWAXS measurements were performed on beamline ID09 at the European Synchrotron Radiation Facility (ESRF, Grenoble). The experimental setup is described in the literature,⁶⁴ whereas the specific details of the present study are summarized in the ESI.† All scattering patterns were measured with the FReLoN area detector,⁶⁵ azimuthally integrated and reduced to difference scattering curves $\Delta S(q, t)$ (with t being the time delay between the laser and X-ray pulses, $q = (4\pi/\lambda)\sin(2\theta/2)$ with λ and 2θ being the X-ray wavelength and the scattering angle respectively) according to standard procedures.^{66,67} To follow the structural dynamics of $[\text{Fe}(\text{btbip})_2]^{2+}$ in a 9 mM MeCN solution, the data was collected in two separate runs using different X-ray energies, 25.2 keV and 18 keV. By using a multi-layer monochromator, the X-ray energy bandwidth of the undulator harmonics were reduced to 1.55% and 1.9% for the 25.2 keV and 18 keV runs respectively, which greatly enhances the structural sensitivity compared to the conventional raw undulator pink beam measurements while maintaining high X-ray flux.⁶⁷ Note that using high energy X-rays gives access to a wider range of scattering vectors q , allowing for a more precise structural analysis.⁶⁸ The higher X-ray flux and detector efficiency at 18 keV made the 18 keV measurements four times faster per time delay than at 25.2 keV. The 18 keV dataset was therefore acquired with more laser/X-ray time delays to better resolve the excited state kinetics of the molecule. By contrast, the 25.2 keV run was done with only one time delay, 150 ps, in order to obtain the best possible structural refinement of the MC state.

The interpretation of the TRWAXS data was conducted according to the established framework,⁶⁹ where the experimental curves are fitted with theoretical signals from three contributions: the changes in the solute structure, solvation shell rearrangements (also referred to as the cage term) and the changes in the bulk solvent structure as a result of (adiabatic) heating. We note that the inclusion of the density change component in the solvent response did not improve the fits in the time range 0–400 ps (see ESI†) unlike in recent work on aqueous solutions of similar Fe^{II} complexes.^{29,70} The analysis is based on structural models of the complex and the surrounding

solvation shell (cage term) which were calculated by DFT and classical molecular dynamics (MD) simulations, respectively. The difference signal for the bulk solvent temperature increase was measured according to the standard procedure using azobenzene molecules.⁷¹ The details of the analysis and the theoretical calculations are described in the ESI.†

Results and discussion

Since the MLCT state of $[\text{Fe}(\text{btbip})_2]^{2+}$ has been shown to decay on the 300 fs time scale, the relevant states for 100 ps time-resolved experiments are the GS, ^3MC , and ^5MC states. The structure of these states were fully relaxed with no symmetry constraints, allowing for all possible Jahn–Teller effects, using the PBE0 (ref. 72–74) functional and a triple- ζ basis set^{75–77}

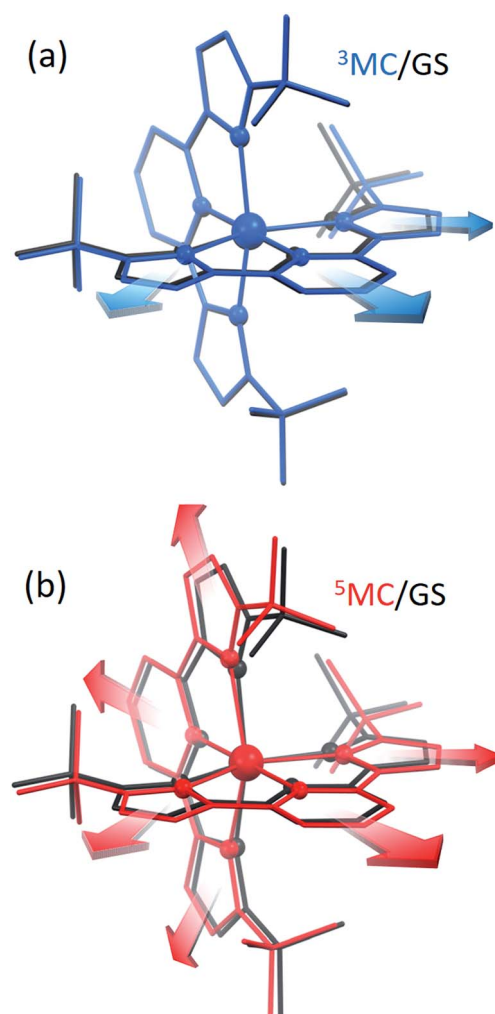


Fig. 2 (a) Overlay of the $[\text{Fe}(\text{btbip})_2]^{2+}$ structure in the ^3MC (blue) and GS (black) states. Arrows show that one of the ligands is preferentially repelled from Fe in ^3MC compared to the GS. (b) Overlay of the $[\text{Fe}(\text{btbip})_2]^{2+}$ structure in the ^5MC (red) and GS (black) states. Arrows show that both ligands are equally repelled from Fe in ^5MC compared to GS. In both (a and b) the spheres represent Fe and its first coordination shell, rods represent the rest of the molecular structure. The hydrogens are omitted for clarity.

which is known to give good structural results for Fe–NHC complexes.^{45,46} A continuum model⁷⁸ for the MeCN solvent was used to simulate the solvent conditions and to provide charge screening for the metal complexes. The changes in the structure of the complex in the ³MC and the ⁵MC states compared to the GS are shown in Fig. 2. The structure of [Fe(btbp)₂]²⁺ in the three states is parameterized by two bond lengths,⁷⁹ namely the axial Fe–N_{Py} (*R*_{ax}) and equatorial Fe–C_{NHC} (*R*_{eq}) bond lengths (Fig. 1). Their values are summarized in Table 1. The calculated GS (*t*_{2g})⁶ (for convenience we use the notation for the O_h symmetry) structure of [Fe(btbp)₂]²⁺ is in good agreement with X-ray crystallographic data⁴⁹ and is characterized by a distorted octahedral configuration around the Fe^{II} center, with *R*_{ax} (1.935 Å) being shorter than *R*_{eq} (2.10 Å). The calculated ³MC (*t*_{2g})⁵(*e*_g)¹ state has one ligand further away than the other, as only one anti-bonding *e*_g orbital is populated (further discussions in ESI†). Specifically, the *R*_{eq} and *R*_{ax} bond of the first ligand are elongated by ~0.2 Å, whereas *R*_{ax} of the second ligand is elongated by ~0.1 Å. In the ⁵MC (*t*_{2g})⁴(*e*_g)² state, where two antibonding orbitals are occupied, both ligands are repelled equally from the Fe center by ~0.3 Å and ~0.2 Å for *R*_{ax} and *R*_{eq}, respectively.

Fig. 3a shows a comparison of the calculated ³MC and ⁵MC signals fitted to the 25.2 keV data recorded 150 ps after laser excitation. The ⁵MC signal gives the best fit with a χ^2 value of 1.70 compared with 1.88 for ³MC in agreement with previous assignments.^{49,50} Fig. 3b shows the components used for fitting the data. The minor discrepancy between the data and the fit in the range 1.5–2.0 Å^{−1} might be due to the simplified description of the cage term in the classical MD simulation. The cage term was simulated with a purely classical MD, which accounts for solvation effects arising from the structural changes in the molecule, but it neglects the electronic charge redistribution in the molecule from the GS to ⁵MC. This effect is included in *ab initio* MD simulations and, as was shown for aqueous [Fe(bpy)₃]²⁺,⁸⁰ gives a more significant reorganization of the solvation shell. Constraining the fit to the high-*q* range of the data (*q* > 2.5 Å^{−1}), where the cage term is insignificant, increases the contrast between the ³MC and ⁵MC states from a statistical point of view giving χ^2 values of 1.03 and 1.56 for ⁵MC and ³MC,

respectively. This further supports the excited state assignment as ⁵MC (see ESI†).

The structural refinement of the excited states of [Fe(btbp)₂]²⁺ is non-trivial due to its many degrees of freedom and the (near) similar scattering power of the Fe/C and Fe/N atom pairs that dominate the signal in the high-*q* range. An individual refinement of all pairs of interatomic distances would significantly exceed the maximal number of parameters that can reliably be inferred from the TRWAXS signal.^{67,68} Thus, we have developed a model where the key interatomic distances are used to define the structure of the rest of the molecule. By varying these parameters and from those determine the resulting changes to the rest of the structure, one can refine the overall molecular structure within the framework of the proposed structural model. The key is that the parameters chosen need to define the relevant reaction coordinates associated with the structural dynamics.

Previous work on Fe^{II} SCO complexes have established that the structural changes induced by the transition from the GS to ⁵MC are well described by parameterizing the global structure through parameters that define the shape of the first Fe coordination shell, including metal–ligand bond lengths, ligand bite angles and ligand rocking angles, as the reaction coordinates.^{22–40,81–86} For example, the structural dynamics from the spin transitions in [Fe(terpy)₂]²⁺ – which is structurally similar to [Fe(btbp)₂]²⁺ – were successfully described by including only the axial bond length and the bending angle of the ligand as

Table 1 Energies and structural parameters of the first coordination shell of Fe in [Fe(btbp)₂]²⁺ for the GS, ³MC, and ⁵MC states obtained from the DFT calculations and from the refinement of the ⁵MC state in the experiment

	GS (¹ MC)		³ MC	⁵ MC	
	Calc.	Exp. ^c	Calc.	Calc.	Exp.
<i>E</i> (eV) ^a	0	0	0.95	0.72	0.75 ± 0.15
<i>R</i> _{ax} (Å) ^b , (Fe–N _{Py})	1.94	1.939	2.04 (I) ^d 2.17 (II) ^d	2.23	2.23 ± 0.03
<i>R</i> _{eq} (Å) ^b , (Fe–C _{NHC})	2.10	2.096	2.13 (I) ^d 2.29 (II) ^d	2.32	2.31 ± 0.02

^a Calculated using B3LYP*/6-311G(d,p)/PCM(MeCN). ^b Calculated using PBE0/6-311G(d,p)/PCM(MeCN). The standard deviation of the calculated bond lengths was found to be 0.001 Å. ^c From crystallographic data in ref. 49. ^d Marks I and II correspond to the ligand numbering.

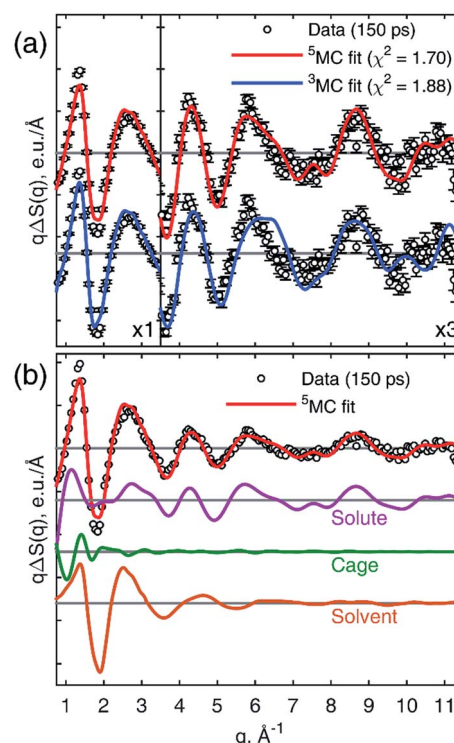


Fig. 3 (a) Fits of the structural models for the ³MC and ⁵MC states to the TRWAXS data collected with 25.2 keV X-rays at 150 ps time delay. The vertical scale of right sub-panel is multiplied by 3 for *q* > 3.5 Å^{−1}. (b) Decomposition of the ⁵MC model into three contributions: solute, cage and solvent.



reaction coordinates.^{26–29} In recent TRWAXS measurements on $[\text{Co}(\text{terpy})_2]^{2+}$, the excited state refinement was done using the axial bond length as the fitting parameter while maintaining the ratio between the axial and equatorial bond length constant.⁷⁹ Since there is redundancy in any chosen set of coordinates, as they are interrelated (e.g. changing bond angles often results in changes to metal–ligand bond lengths), we have chosen the fewest coordinates possible that describe the fully relaxed minima to avoid overfitting. In the case of $[\text{Fe}(\text{btbip})_2]^{2+}$ we choose the axial bond length R_{ax} and the equatorial one R_{eq} – which combined define the bending angle of the ligand – as the two independent reaction coordinates. This choice is based on the sensitivity of TRWAXS: the largest contribution to the high- q signal is from the Fe–N_{Py} and Fe–C_{NHC} pairs which makes them the natural parameters in the fitting procedure. To map the overall atomic positions characterized by the selected structural parameters, we have implemented a procedure based on the interpolation between the structures produced by varying the values of R_{ax} and R_{eq} and performing constrained DFT for each (R_{ax} , R_{eq}) point. Details of the DFT calculations and the associated structural fitting procedure are summarized in the ESI†

The refined structure of $[\text{Fe}(\text{btbip})_2]^{2+}$ in the ^5MC state is obtained by fitting the data in the high- q range ($q \geq 2.5 \text{ \AA}^{-1}$) according to the model described above, with the DFT-optimized ^5MC state ($R_{\text{ax}} = 2.231 \text{ \AA}$, $R_{\text{eq}} = 2.317 \text{ \AA}$) as a starting geometry. The result of the refinement is: $R_{\text{ax}} = 2.23 \pm 0.03 \text{ \AA}$ and $R_{\text{eq}} = 2.31 \pm 0.02 \text{ \AA}$ (Table 1). The good agreement between the theoretically optimized ^5MC structure and the experimentally fitted structure validates the DFT method (PBE0/6-311G(d,p)/PCM(MeCN)) to predict excited state structures in (quasi) equilibrium. Note that our refinement procedure allows for an experimental determination of the global molecular structure as a function of two bond distances rather than the refinement of these two distances alone. Moreover, the method employed here can be used for the refinement of many organometallic complexes which do not contain pairs of heavy atoms. While the latter has been traditionally seen as a necessary condition for the structural refinement using TRWAXS,^{87–95} the present work, together with the recent experiments on $[\text{Co}(\text{terpy})_2]^{2+}$,⁷⁹ extend the applicability of the TRWAXS technique significantly.

The many time points in the 18 keV dataset were used to analyze the excited state kinetics of $[\text{Fe}(\text{btbip})_2]^{2+}$. Here we used the global fit approach,^{66,69} which ties the reaction kinetics to the hydrodynamic state of the liquid *via* the conservation of mass and energy (see ESI† for details). Fig. 4a shows a comparison of the fitted theoretical and experimental $\Delta S(q,t)$ curves for a subset of time points. For all time points we find a very good agreement between the experimental data and the model fit. This is also the case when comparing the global fit of the excited state fraction $\gamma(t)$ and the solvent temperature $\Delta T(t)$ to the values obtained from fits of the individual time points (Fig. 4b and c). From the global fitting we find that immediately ($\ll 100$ ps) after the excitation event, $35 \pm 1\%$ of the $[\text{Fe}(\text{btbip})_2]^{2+}$ molecules in the probed sample volume arrive in the ^5MC state within the 100 ps time resolution of the experiment. This is followed by the decay of the ^5MC to the GS with a time constant of 260 ± 10 ps, in fair agreement with the 230 ps lifetime

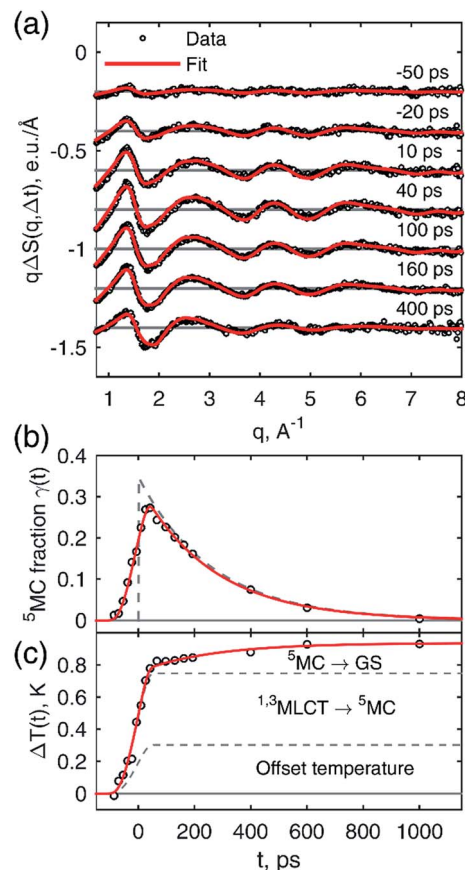


Fig. 4 (a) Results of the global fitting of the representative set of curves from the 18 keV data. (b) Population dynamics of the ^5MC state. Black circles represent the results of the individual fit of each time point; red line represents the result of the global fitting of the entire data set; the dashed line represents the un-convoluted ^5MC population dynamics. (c) Temperature dynamics. Dashed lines separate the three main contributions to the temperature rise as discussed in the main text.

obtained from optical spectroscopy.⁴⁹ The temperature increase of the bulk solvent is tied to the solute excited state population dynamics, with a prompt increase followed by further growth on the 260 ps time scale. The sharp temperature rise appears around time zero and is partly due to fast relaxation from the MLCT to ^5MC (perhaps through a short lived ^3MC intermediate⁵⁰) and the associated redistribution of most of the photon energy into the solvent. A fraction of the initial solvent temperature increase could not be attributed to the relaxation of the excited molecules as discussed further below. After 100 ps the temperature grows due to the release of the ^5MC state energy following its decay to the GS. The three contributions to the temperature dynamics are shown in Fig. 4c.

After thermal relaxation of the excited species we observe a temperature rise of 0.94 K. Considering the initial excitation fraction, 35%, and the amount of energy dissipated into the solvent from photon absorption, we expect a 0.64 K temperature rise. The difference, 0.3 K, comes from an unknown source. Considering the relatively low laser fluence (0.052 J cm^{-2}) and the relatively long laser pulse, 1.2 ps (FWHM), we can exclude

multi-photon excitation of the solvent as the additional heat source. To verify this, we performed TRWAXS measurements on neat MeCN under similar experimental conditions and did not observe any detectable signal. The 0.3 K temperature rise might point towards an ultrafast deactivation ($\ll 100$ ps) of the MLCT state to the GS, for example *via* an intermediate MC-like state such as ^3MC . We estimate that an additional $17 \pm 1\%$ of excited solute molecules could relax in this way, corresponding to a total excited state fraction of $52 \pm 1\%$. We note that the excited state fraction and temperature rise are in fair agreement with the expected values of 58% and 1.06 K, respectively, calculated using the laser fluence, X-ray beam size and optical density (see ESI† for more details). Understanding the nature of the observed temperature offset requires better time resolution which is beyond the scope of the present study.

Based on the simple kinetics and the clear observation of the temperature rise from the decay of the ^5MC , the energy difference between the ^5MC and GS states ΔE can be determined. Although the $^5\text{MC} \rightarrow \text{GS}$ relaxation and the corresponding temperature rise were discussed in the TRWAXS work on $[\text{Fe}(\text{bpy})_3]^{2+}$,^{70,96} this work represents the first determination of the complex's energy in the vibrationally relaxed ^5MC state, to the best of our knowledge. After incorporation of the energy difference into the global fitting procedure, we arrive at a value of $\Delta E = 0.75 \pm 0.15$ eV (see ESI† for details). While DFT is known to give robust structural information for organometallic complexes, irrespective of the functional choice, the sensitivity of the calculated ^5MC energy on the choice of the functional has previously been seen for other Fe high spin/low spin complexes. In particular, the amount of the Hartree–Fock exchange used in hybrid functionals can significantly impact the calculated energy of the same geometry.^{97,98} Thus, we compared PBE0,^{72–74} PBE0-D3,⁹⁹ B3LYP,¹⁰⁰ B3LYP*,^{101,102} CAMB3LYP,¹⁰³ and TPSS^{104–106} calculated energies with the experimental information about the ^5MC state energy. The calculated energy of the ^5MC state was found to depend significantly on the choice of functional, with the B3LYP* energy of 0.72 eV in significantly better agreement with the experimental result compared to the PBE0 energy of 0.14 eV. At the same time, DFT optimizations using these two functionals were found to give very similar geometries for the structure of the ^5MC state, that are also in good agreement with the experiments (further details in ESI†). It is interesting to note that in terms of energy levels, B3LYP* gives the best agreement with the experiment among the functionals tested here for this short-lived intermediate, similar to what was previously observed in other Fe^{II} high and low spin complexes.⁹⁷ While the present results for $[\text{Fe}(\text{btbip})_2]^{2+}$ are limited in scope, they point to encouraging prospects to use a combination of TRWAXS and DFT to provide a reliable understanding of the potential energy landscape in these kinds of photosensitizers that have otherwise often been difficult to characterize.

Combining the structural and energetic data obtained here, the complete photocycle of $[\text{Fe}(\text{btbip})_2]^{2+}$, from the initial photoexcitation to ground state recombination, is presented in Fig. 5. The experimentally determined values for the bond lengths and the energy levels are summarized in Table 1. As was

initially suggested by optical spectroscopy,⁴⁹ the excited state behavior of $[\text{Fe}(\text{btbip})_2]^{2+}$ is similar to that of other Fe^{II} polypyridine complexes: upon excitation to MLCT, the complex quickly undergoes intersystem crossing and ultimately ends up in a longer lived ^5MC state. In spite of the short MC state lifetime of <300 ps, we find that the LFS of $[\text{Fe}(\text{btbip})_2]^{2+}$ is not strong enough to alter the MLCT deactivation pathway such that it would proceed to the GS by only populating the ^3MC intermediate. This finding indicates that, at least for NHC systems, the short MC state lifetime is not indicative of its ^3MC character, as suggested for expanded cage and push–pull compounds in recent spectroscopic works^{54,55} and observed in weak LFS Ru^{II} based compounds.^{56–58} However, the structural rearrangements upon relaxation to the ^5MC state have unusually large amplitudes as compared to similar Fe^{II} complexes. For $[\text{Fe}(\text{bpy})_3]^{2+}$ and $[\text{Fe}(\text{terpy})_2]^{2+}$, the Fe–N bonds expand isotropically by 0.22 Å,^{27,28} but in the case of $[\text{Fe}(\text{btbip})_2]^{2+}$, the axial R_{ax} and equatorial R_{eq} bonds expand by 0.29 Å and 0.21 Å, respectively. Recent computational results on complexes with NHC and CN[−] ligands suggest that the increase in the ligand field results in pushing the excited state minima away from the GS minima along the metal-to-ligand bond length reaction coordinate.^{42,45,46} The structure of $[\text{Fe}(\text{btbip})_2]^{2+}$ in its ^5MC state observed here confirms this trend and illustrates the effect of the σ -donating carbene ligands on the excited states structure of the complex. Interestingly, for the sister compound $[\text{Fe}(\text{bmip})_2]^{2+}$, which suffers less from steric hindrance than $[\text{Fe}(\text{btbip})_2]^{2+}$ due to its smaller Me side groups, calculations suggest even larger extensions of the ^5MC state, 0.34 Å and 0.25 Å for ΔR_{ax} and ΔR_{eq} , respectively.⁴⁵ Since the predicted bond lengths in the relaxed ^5MC states of both $[\text{Fe}(\text{btbip})_2]^{2+}$ and $[\text{Fe}(\text{bmip})_2]^{2+}$ are very similar, the increase in ΔR_{ax} and ΔR_{eq} can largely be ascribed to the shorter initial R_{eq} (~ 0.1 Å) bond length in the ground state of $[\text{Fe}(\text{bmip})_2]^{2+}$.⁴⁵

These observations provide the first unambiguous characterization of the excited MC state of an Fe-centered system with properties falling between those of traditional Fe^{II} SCO

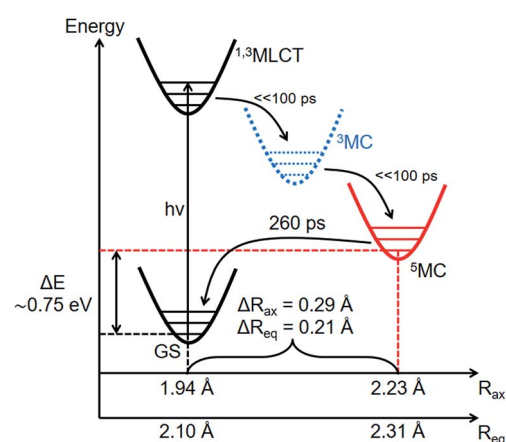
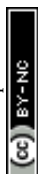


Fig. 5 Energy level scheme of $[\text{Fe}(\text{btbip})_2]^{2+}$ based on the experimental results of this work. Although the ^3MC state was not observed, it was added to the relaxation cascade analogously to Fe^{II} polypyridyl complexes.



complexes and strong LFS complexes utilizing NHC ligands with increased MLCT lifetimes. It confirms the computational prediction that NHC compounds exhibit excited MC states where the minima are pushed further away from the GS along the main reaction coordinate (metal-to-ligand bond distance). Together with energy destabilization, this structural distortion of the scavenger MC states shortens their lifetime, and make them less accessible from the MLCT manifold, which in turn results in increased MLCT lifetimes. Hence, $[\text{Fe}(\text{btbip})_2]^{2+}$ exhibits stronger geometric distortion in the ^5MC state compared to traditional SCO systems; at the same time, the energy and structural distortion of the MC states are not large enough to remove the ^5MC state from the MLCT deactivation cascade. Overall, the presented results show that the transition in photophysical properties between weak LFS and strong LFS Fe–NHC compounds manifest itself not only in the destabilization of the MC states, but also in the significantly different structural dynamics of these systems.

Conclusion

To summarize, the excited state relaxation following the MLCT excitation of $[\text{Fe}(\text{btbip})_2]^{2+}$ was probed by TRWAXS with 100 ps time-resolution, allowing for the definite assignment of a 260 ps lifetime metal-centered quintet excited state as part of the MLCT relaxation pathway. The structural analysis of the excited state demonstrates that the ^5MC state is significantly distorted compared to the GS, which is observed as unusually large differences in metal-to-ligand bond lengths in the two states. Thus, while the $[\text{Fe}(\text{btbip})_2]^{2+}$ photocycle is mechanistically close to that of typical Fe^{II} SCO compounds, the large structural distortion of its ^5MC state distinguishes the complex from traditional Fe^{II} SCO complexes. Since the observed distortion was previously indicated in DFT studies as one of the key factors of the success of the novel NHC compounds, these results provide new experimental insight into the MLCT deactivation pathways of the NHC family. We note that the combination of bulky *t*Bu side-groups with the strong σ -donating NHC ligands allowed us to probe an interesting part of the excited state cascade that previously was inaccessible in related NHC complexes. These results are of fundamental interest in the context of recent discussions of the nature of short-lived MC states in Fe^{II} complexes with strong LFS.^{54,55} Overall, this work suggests that a characterization of the full deactivation cascade in other complexes with few-100 ps and faster GS recovery is necessary to fully characterize the rich and non-trivial photo-physics of Fe complexes.

More generally this work illustrates how TRWAXS on a photosensitive molecule in solution provides information not only on the transient structures, but also on the energies of short-lived excited species, which is traditionally a difficult task since most experiments are either tailored towards structure or energy sensitivity. The refinement procedure aided by DFT calculations used in this work will further expand the classes of systems for which TRWAXS can provide experimental determination of short-lived excited state structures, beyond systems with heavy atom pairs. We note that a key enabling factor in the

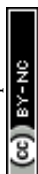
direct identification of the ^5MC state and in the high precision structural refinement is the availability of high-quality quasi-monochromatic TRWAXS data up to large scattering vectors, $q_{\text{max}} = 11.5 \text{ \AA}^{-1}$. Moreover, TRWAXS can uniquely provide information about excited state energies by direct assessment of the amount of energy disposed into the solvent during excited state relaxation. Such information cannot be readily retrieved for MC states with optical methods, such as absorption or fluorescence spectroscopy due to the formally dipole-forbidden nature of the optical transitions between the GS and MC states which drastically reduces the interaction cross-section and, more importantly, because the relaxed MC states are geometrically inaccessible from vertical light excitations (Fig. 5). While the ΔE value obtained in this work is subject to some uncertainty, coupled with the advanced structural analysis, it provides an important stepping-stone for much more comprehensive explorations of excited state potential energy surfaces. Further improvements of the experimental setup in terms of stability and signal-to-noise should help in increasing the precision of the extracted energies. Additionally, careful investigation of the power, concentration and pump wavelength effects should make the quantification of ΔE more robust. Improvements in the cage modelling will also impact the accuracy of the energetic parameters since both solvation and solvent contributions are present primarily in the low- q region of the difference signal. The experimental quantification of the energy and structure of the short-lived ^5MC state of $[\text{Fe}(\text{btbip})_2]^{2+}$, provides a robust experimental tool for the direct validation and comparison of different quantum chemical methods, in particular the choice of functionals, to accurately predict the structure and energy of short-lived MC states in Fe complexes. Future systematic TRWAXS studies of Fe^{II} complexes will be able to capture the effect of the ligand structure on the kinetic, structural, and energetic aspects of charge transfer and spin transitions in this class of systems allowing for more detailed investigations of the role of the excited MC states in the MLCT deactivation process. This combined progress in experimental and theoretical capabilities will benefit not only the search for perspective earth-abundant photosensitizers, but also the advancement in the understanding of SCO compounds for future opto-magnetic materials.

Conflicts of interest

There are no conflicts to declare.

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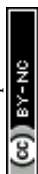
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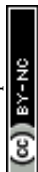
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Paper II

Anisotropy enhanced X-ray scattering from solvated transition metal complexes.

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Anisotropy enhanced X-ray scattering from solvated transition metal complexes

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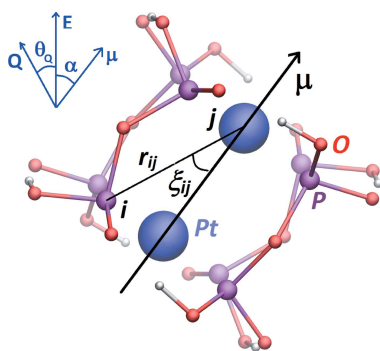
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Time-resolved X-ray scattering patterns from photoexcited molecules in solution are in many cases anisotropic at the ultrafast time scales accessible at X-ray free-electron lasers (XFELs). This anisotropy arises from the interaction of a linearly polarized UV–Vis pump laser pulse with the sample, which induces anisotropic structural changes that can be captured by femtosecond X-ray pulses. In this work, a method for quantitative analysis of the anisotropic scattering signal arising from an ensemble of molecules is described, and it is demonstrated how its use can enhance the structural sensitivity of the time-resolved X-ray scattering experiment. This method is applied on time-resolved X-ray scattering patterns measured upon photoexcitation of a solvated di-platinum complex at an XFEL, and the key parameters involved are explored. It is shown that a combined analysis of the anisotropic and isotropic difference scattering signals in this experiment allows a more precise determination of the main photoinduced structural change in the solute, *i.e.* the change in Pt–Pt bond length, and yields more information on the excitation channels than the analysis of the isotropic scattering only. Finally, it is discussed how the anisotropic transient response of the solvent can enable the determination of key experimental parameters such as the instrument response function.

1. Introduction

Time-resolved X-ray diffuse scattering (XDS) experiments give insight into the photoinduced structural dynamics of solvated molecules. In these experiments, a laser pulse initiates the dynamic process, which is subsequently probed by an X-ray probe pulse arriving at specific time delays after the pump event. If the laser pulse is ultra-short, the ensuing structural dynamics are coherently initiated in the molecular ensemble (Zewail, 2000), and the scattering signal can be used to retrieve structural changes occurring in the molecule after the electronic excitation (Borfecchia *et al.*, 2013; Biasin *et al.*, 2016; Haldrup *et al.*, 2012; Kim *et al.*, 2015a; van Driel *et al.*, 2016; Chergui & Collet, 2017; Kong *et al.*, 2008). Such experiments are of fundamental importance for understanding the structure–function relationship of, for instance, transition metal complexes whose photochemical and photophysical properties can be applied in technologies such as solar energy conversion and photocatalysis (Takeda *et al.*, 2017; Esswein & Nocera, 2007; White, 1982).



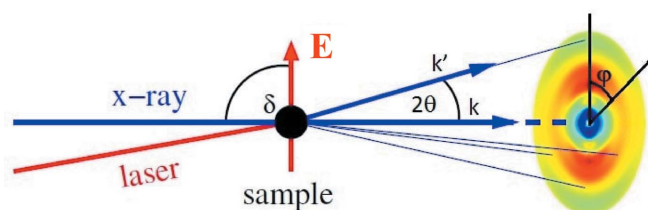


Figure 1

Experimental setup for a standard time-resolved XDS experiment. δ is the angle between the direction of propagation of the X-ray beam and the laser polarization axis $\mathbf{E}$; 2θ is the scattering angle, i.e. the angle between the incoming ($\mathbf{k}$) and outgoing ($\mathbf{k}'$) momentum of the X-ray beam; φ is the angle between the projection of the laser polarization and the scattering vector $\mathbf{Q} = \mathbf{k}' - \mathbf{k}$ on the detector surface.

In typical time-resolved XDS experiments, laser pump and X-ray probe pulses are focused onto a thin liquid jet, which is produced by pumping the liquid sample through a nozzle. The diffuse X-ray scattering is collected on a two-dimensional (2D) detector placed after the sample on the plane perpendicular to the propagation direction of the X-ray beam (Fig. 1). The measured scattering signal contains information about all the inter-nuclear distances of the sample at a specific time delay and it is usually dominated by the scattering from the solvent. The sensitivity to the solute is enhanced in the difference scattering signal, which is constructed by subtracting the signal collected without photoexciting the sample from the signal collected after photoexcitation. In this way the unchanging background contributions cancel out, and the difference scattering signal arises from the changes in the inter-atomic distances in the probed sample volume (Borfecchia *et al.*, 2013; Ihee *et al.*, 2010). The established procedure for analysing scattering data from liquid samples consists of an azimuthal integration of the 2D difference scattering patterns, since the signal is usually assumed to arise from an isotropically distributed ensemble of molecules (Ihee *et al.*, 2010; Haldrup *et al.*, 2010). If the sample is isotropic, the azimuthal integration allows for an improvement of the signal-to-noise (S/N) without loss of information. This procedure was first established with synchrotron data and it is justified when the time resolution is longer than the molecular rotational correlation time in solution, which ranges in the 10–100 ps time scale for transition metal complexes (Lakowicz, 2006; Kim *et al.*, 2015b).

At X-ray free-electron lasers (XFELs), that can deliver femtosecond X-ray pulses, the photoinduced structural changes in the sample can be captured at the time scale of atomic motions. This enables the observation of vibrational and rotational molecular dynamics in, for instance, solvated transition metal complexes (Biasin *et al.*, 2016; Kim *et al.*, 2015b; Lemke *et al.*, 2017; Chergui & Collet, 2017). If the

photoselection process (illustrated in Fig. 2 and further described below) creates an aligned excited-state ensemble of molecules, anisotropic 2D scattering patterns can be observed on time scales shorter than the rotational correlation time of the molecules (Kim *et al.*, 2011; Kim *et al.*, 2015b; Yang *et al.*, 2016a,b; Glowina *et al.*, 2016). Anisotropic scattering patterns contain information on the molecular preferred orientation, and thus can add sensitivity to spatial degrees of freedom compared with isotropic patterns (Hensley *et al.*, 2012; Burger *et al.*, 2010; Küpper *et al.*, 2014). The theoretical foundation for interpreting anisotropic scattering contributions from aligned ensembles of molecules in time-resolved experiments has been laid out in some detail over the past ten years (Baskin & Zewail, 2006; Lorenz *et al.*, 2010; Brinkmann & Hub, 2015; Penfold *et al.*, 2012). However, quantitative structural analysis of anisotropic scattering data from molecular ensembles where a photoselected sub-population has been promoted to an electronic excited state has been demonstrated only in a very few cases in the gas phase (Yang *et al.*, 2016a,b; Glowina *et al.*, 2016), and a robust methodology for such cannot yet be said to have been fully established as the debate surrounding the work of Glowina *et al.* shows (Bennett *et al.*, 2017; Glowina *et al.*, 2017). Specifically with respect to solution-state molecular systems, only qualitative analysis of time-resolved anisotropic scattering data have been reported, and the anisotropic contributions to the observed scattering patterns have been mostly used only to obtain the rotational correlation time of the molecules in solution (Kim *et al.*, 2011; Kim *et al.*, 2015b).

In this article, we revisit the formalism derived by Lorenz *et al.* (2010) for analysing scattering from a photo-aligned ensemble of molecules. We use this formalism to extract the isotropic and anisotropic contribution from 2D scattering patterns measured at an XFEL upon photoexcitation of a transition metal complex in solution and we explore a few of the key parameters involved in this procedure. We show that, in the presence of anisotropic scattering, the separation of the two contributions can, and should, replace the standard azimuthal integration in the data reduction procedures. As a key point, we demonstrate that the anisotropic contribution

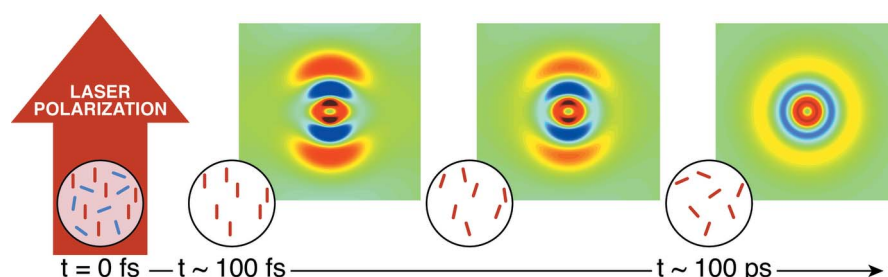


Figure 2

Illustration of the photoselection process. Before the arrival of the laser pump ($t < 0$), the molecules are randomly oriented in solution. The laser pulse preferentially excites the molecules with the transition dipole moments parallel to the laser polarization axis. Thus, the excited-state population is created as an aligned ensemble (at $t = 0$ the distribution of the transition dipole moment in molecules being excited is a cosine-squared distribution with respect to the laser polarization axis) yielding anisotropic difference scattering patterns. After the excitation event ($t > 0$), the rotation of both the excited and unexcited populations causes rotational dephasing of the alignment.

can be quantitatively analysed in order to extract structural information about the photoexcited ensemble of molecules. These results are discussed in the framework of how the information extracted from a combined analysis of the isotropic and anisotropic contributions to the measured difference scattering signals can potentially help disentangle the many inter- and intra-nuclear degrees of freedom involved in photoinduced structural dynamics of molecules in solution.

The method is exemplified on scattering data collected at the X-ray Pump Probe (XPP) instrument (Chollet *et al.*, 2015) at the Linac Coherent Light Source upon photoexcitation of the tetrakis- μ -pyrophosphitodiplatinate(II) ion $[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]^{4-}$, here abbreviated as PtPOP. Fig. 3 shows the molecular structure of PtPOP: a Pt–Pt dimer is held together by four pyrophosphito ligands. The compound belongs to the C_{4h} point group, with approximately fourfold symmetry along the Pt–Pt axis (Zipp, 1988; Gray *et al.*, 2017). Thus, the Pt–Pt axis has higher rotational symmetry than the other two axes, and the molecule is a symmetric top (*i.e.* two principal moments of inertia have the same value and the third has a unique value). This compound was first synthesized in 1977 and has been the subject of a vast amount of studies, due to its characteristic photophysical properties and activity as a photocatalyst (Roundhill *et al.*, 1989; Stiegman *et al.*, 1987). In the last decades, PtPOP has become a model compound for time-resolved X-ray studies, due to its high scattering power, its long singlet excited-state lifetime, and its high symmetry (Christensen *et al.*, 2009; van der Veen *et al.*, 2009). For this experiment, an 80 mM aqueous solution of PtPOP was circulated through a nozzle producing a 50 μm round liquid jet. Each photocycle was initiated by a 3 μJ laser pulse at 395 nm and with 50 fs pulse width (FWHM), focused onto a

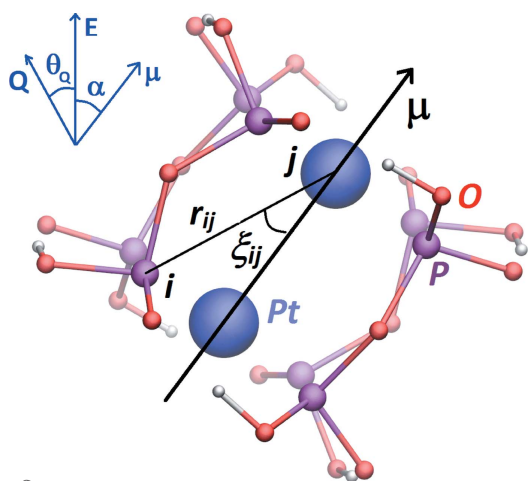


Figure 3

Molecular structure of PtPOP and relevant angles. PtPOP is a symmetric top molecule with the main axis of symmetry parallel to the Pt–Pt axis (Zipp, 1988; Gray *et al.*, 2017). In the molecular fixed frame (black arrows): ξ_{ij} is the angle between the internuclear displacement $\mathbf{r}_{ij}$ and the transition dipole moment $\boldsymbol{\mu}$ of the molecule, which is parallel to the main axis of symmetry of the molecule. In the laboratory frame (blue arrows): α is the angle between the laser polarization axis $\mathbf{E}$ and the transition dipole vector $\boldsymbol{\mu}$ of the molecule, θ_Q is the angle between the laser polarization axis and the scattering vector.

150 μm -diameter spot. The scattering from the 9.5 keV X-ray probe pulses was detected by the Cornell–SLAC Pixel Array Detector (CSPAD) (Philipp *et al.*, 2011) covering scattering vectors up to 4.5 $\text{\AA}^{-1}$. The time delay t between the laser and the X-ray pulses was determined for every pump–probe event with ~ 10 fs (FWHM) resolution using the XPP timing-tool (Minitti *et al.*, 2015). The detector signal was corrected according to the procedure described by van Driel *et al.* (2015), including corrections for the detector geometry and the horizontal polarization of the X-ray beam. The corrected scattering signal was scaled to the liquid unit cell reflecting the stoichiometry of the sample (Haldrup *et al.*, 2010), yielding the acquired signal in electron units per solute molecule (e.u. molec^{-1}). Individual 2D difference scattering patterns were then time-sorted and averaged. Movie S1 of the supporting information shows averaged measured difference scattering patterns upon photoexcitation of PtPOP as a function of increasing time delay: a strongly anisotropic difference scattering signal is visible at an early time delay and decays on a ~ 100 ps time scale. The signal is expected to arise predominantly from the shortening of the Pt–Pt distance since the 395 nm transition, which has polarization along the Pt–Pt bond, involves the promotion of an electron from the anti-bonding $d\sigma^*$ to the bonding $p\sigma$ orbital (Stiegman *et al.*, 1987). Christensen *et al.* investigated the structure of the excited state of PtPOP in water with time-resolved XDS and obtained a Pt–Pt contraction of 0.24 ± 0.06 $\text{\AA}$ with respect to the ground state of the molecule (Christensen *et al.*, 2009). van der Veen *et al.* concluded a 0.31 ± 0.05 $\text{\AA}$ Pt–Pt contraction upon excitation of the complex in ethanol, with X-ray absorption spectroscopy (van der Veen *et al.*, 2009). The well defined transition dipole moment and the strong scattering signal arising from the contraction of the Pt–Pt bond makes PtPOP an ideal model system to benchmark the formalism required in order to interpret anisotropic difference scattering patterns.

2. Methods

In time-resolved XDS experiments, the molecules in solution are randomly oriented before the arrival of the laser pump. If the linearly polarized ultrashort laser pulse interacts with a single transition dipole moment $\boldsymbol{\mu}$ of the molecule, the angular distribution D of this transition dipole moment in molecules being excited displays cylindrical symmetry with respect to the laser polarization $\mathbf{E}$. Therefore, this distribution can be expressed through an expansion in Legendre polynomials $P_n(\cos \alpha)$ of only the angle α between the laser polarization axis and the transition dipole moment (Baskin & Zewail, 2006),

$$D(\alpha, \eta) = D(\alpha) = \sum_{n=0}^{\infty} c_n P_n(\cos \alpha), \quad (1)$$

where α and η are the polar and azimuthal angles, respectively, in a spherical coordinates system with polar axis $\mathbf{E}$, and c_n are expansion coefficients. In the case of one-photon absorption of linearly polarized radiation by an isotropic molecular

ensemble in thermal equilibrium, the distribution of the transition dipole moment in molecules being excited is a cosine-squared distribution with respect to the laser polarization axis (Møller & Henriksen, 2012; Baskin & Zewail, 2006). Cast into the generic form of equation (1), the distribution of excited-state molecules immediately after the excitation event can be expressed as a sum of two terms,

$$D(\alpha) = c_0 P_0(\cos \alpha) + c_2 P_2(\cos \alpha), \quad (2)$$

where $P_0(x) = 1$ and $P_2(x) = (3x^2 - 1)/2$, with $c_2 = 2c_0$. Properly normalizing (Kleef & Powis, 1999) the angular distribution in equation (1) on unit sphere gives

$$1 = \frac{1}{2} \int_0^\pi D(\alpha) \sin \alpha \, d\alpha = c_0, \quad (3)$$

where the last equality is a consequence of the orthogonality of the Legendre polynomials.

Assuming ultrashort laser pump and X-ray probe pulses, the differential scattering cross section from an ensemble of excited molecules, at a specific pump–probe delay time t , can be expressed by weighting the squared molecular form factor with the instantaneous distribution ρ of nuclear geometries (Lorenz *et al.*, 2010),

$$\frac{d\sigma}{d\Omega}(\mathbf{Q}, t) = \sigma_T \int d\mathbf{R} \rho(\mathbf{R}, t) |F_{\text{mol}}(\mathbf{Q}, \mathbf{R})|^2, \quad (4)$$

where $\mathbf{R}$ has dimensions $3N$ and describes the nuclear coordinates in the laboratory frame, σ_T is the Thomson scattering cross section and $\mathbf{Q}$ is the scattering vector. After assuming that rotational and vibrational degrees of freedom of the molecule are uncoupled (Lorenz *et al.*, 2010), we express the rotational part of the distribution through $D(\alpha)$ in equation (1) and the vibrational distribution as a δ -distribution. Under these assumptions, the scattering from an ensemble of molecules with their transition dipole moments aligned with respect to the laser polarization axis can be calculated through

$$\frac{d\sigma}{d\Omega}(\mathbf{Q}, t) = 2\pi\sigma_T \int_0^\pi d\alpha \sin \alpha D(\alpha, t) |F_{\text{mol}}[\mathbf{Q}, \alpha, \mathbf{r}(t)]|^2, \quad (5)$$

where $\mathbf{r}$ is the vector of inter-nuclear distances. Furthermore, this expression [equation (5)] can be simplified by utilizing the fact that the molecule is a symmetric top with the transition dipole moment parallel to the unique axis of symmetry. Under this assumption, as detailed by Baskin & Zewail (2005), the angular distribution of each intra-molecular distance $\mathbf{r}_{ij}$ with respect to the laser polarization axis can be expressed through the angle ξ_{ij} between $\mathbf{r}_{ij}$ and the main axis of symmetry of the molecule. These parameters are illustrated in Fig. 3: PtPOP is a symmetric top molecule with the main axis of symmetry parallel to the Pt–Pt bond, which is also the direction of the transition dipole moment photoselected in this experiment and therefore meets the above assumptions. As described by Lorenz *et al.* (2010), under the described assumptions, the integral in equation (5) has the analytical form

$$\frac{d\sigma}{d\Omega}(\mathbf{Q}, \theta_Q, t) = 2(2\pi)^2 \sigma_T \sum_n P_n(\cos \theta_Q) S_n(\mathbf{Q}, t), \quad (6)$$

where θ_Q is the angle between the laser polarization axis and $\mathbf{Q}$ (see Fig. 3) and

$$S_n(\mathbf{Q}, t) = (-1)^{n/2} c_n(t) \sum_{i,j}^N f_i(\mathbf{Q}) f_j(\mathbf{Q}) P_n[\cos \xi_{ij}(t)] j_n[Qr_{ij}(t)], \quad (7)$$

where j_n are the spherical Bessel functions and f_i is the atomic form factor of atom i , which is used to express the molecular form factor within the independent atom model (Møller & Henriksen, 2012). Assuming one-photon absorption [and thus the angular distribution in equation (2)], only the $n = 0$ and $n = 2$ terms contribute in equation (6) (Lorenz *et al.*, 2010) and the scattering signal can be written as

$$\frac{d\sigma}{d\Omega}(\mathbf{Q}, \theta_Q, t) \propto S_0(\mathbf{Q}, t) + P_2(\cos \theta_Q) S_2(\mathbf{Q}, t). \quad (8)$$

Since $j_0(x) = (\sin x)/x$, S_0 is recognized as the Debye formula for isotropic ensembles,

$$S_0(\mathbf{Q}, t) = \sum_{i,j}^N f_i(\mathbf{Q}) f_j(\mathbf{Q}) \frac{\sin[Qr_{ij}(t)]}{Qr_{ij}(t)}, \quad (9)$$

while S_2 contains information about the orientation of the single bond $\mathbf{r}_{ij}$ with respect to the transition dipole moment of the molecule,

$$S_2(\mathbf{Q}, t) = -c_2(t) \sum_{i,j}^N f_i(\mathbf{Q}) f_j(\mathbf{Q}) P_2[\cos \xi_{ij}(t)] j_2[Qr_{ij}(t)], \quad (10)$$

with $j_2(x) = [(3/x^2) - 1][(\sin x)/x] - 3[(\cos x)/x^2]$. From here, S_0 and S_2 will be referred to as the isotropic and anisotropic part of the scattering signal, respectively. c_2 decays from its initial value of 2 to 0 according to the rotational correlation time of the molecules in solution.

The excitation will leave a hole in the ground-state distribution of the same rotational anisotropy as the excited-state ensemble (Baskin & Zewail, 2006; Jonas *et al.*, 1995). Starting from equation (8), the difference scattering signal ΔS including both excited-state and ground-state contributions can, therefore, be decomposed as (Lorenz *et al.*, 2010)

$$\Delta S(\mathbf{Q}, \theta_Q, t) \propto \Delta S_0(\mathbf{Q}, t) + P_2(\cos \theta_Q) \Delta S_2(\mathbf{Q}, t), \quad (11)$$

where $\Delta S_0(\mathbf{Q}, t)$ and $\Delta S_2(\mathbf{Q}, t)$ are, respectively, the isotropic and anisotropic difference scattering signals arising from the photoinduced structural changes in the sample at a specific pump–probe time delay t .

With respect to equation (11), S_0 and S_2 depend only on internal coordinates of the molecule, while $P_2(\cos \theta_Q)$ depends only on the geometry of the experiment. Specifically, as detailed by Baskin & Zewail (2006), $\cos \theta_Q$ can be expressed as a function of the angles δ , θ and φ , as defined in Fig. 1,

$$\cos \theta_Q = \sin \theta \cos \delta - \cos \theta \cos \varphi \sin \delta. \quad (12)$$

In the case of most standard XDS experiments, and for the PtPOP experiment presented here, the laser beam is nearly

collinear to the X-ray beam. This is one of the possible configurations that yields a 90° angle between the laser polarization axis and the direction of propagation of the X-ray beam (δ in Fig. 1), and equation (12) simplifies to

$$\cos \theta_Q = -\cos \theta \cos \varphi. \quad (13)$$

Since φ is the azimuthal angle on the detector surface, $\cos \theta_Q$ maps P_2 anisotropically onto the detector surface. The second-order Legendre polynomial, and hence the anisotropic contribution to the scattering, vanishes when θ_Q in equation (12) is equal to the magic angle. However, as extensively described by Baskin & Zewail (2006), it is not possible to simultaneously remove anisotropic contributions from the entire scattering pattern for a given choice of δ . The linear relation between scattering intensity and P_2 in equation (11) can be used to retrieve, for a specific Q value, the isotropic and anisotropic difference scattering signal, as described in the following.

Fig. 4 illustrates the extraction of the isotropic and anisotropic difference scattering signals from a difference scattering pattern measured 4.5 ps after the photoexcitation of PtPOP in water. The scattering pattern is shown in Fig. 4(b) and it is

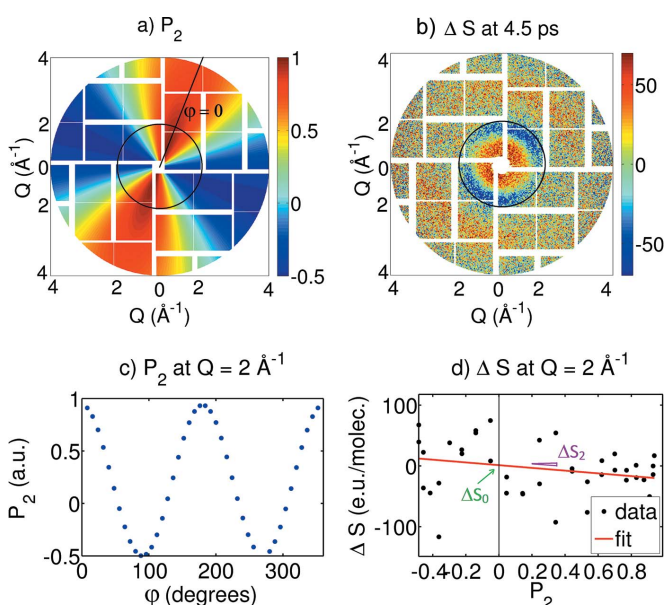


Figure 4
(a) $P_2(\cos \theta_Q)$, with θ_Q as in equation (13), mapped on the CSPAD. The azimuthal angle (φ) is defined to be zero at the projection of the laser polarization axis on the detector surface. A radial bin corresponding to $Q = 2 \text{ \AA}^{-1}$ is selected. (b) Averaged difference scattering pattern at 4.5 ps after photoexcitation of PtPOP in water. For comparison, a full scattering pattern is shown in Fig. S1 of the supporting information. (c) Value of P_2 for the specific radial bin selected in panel (a) as a function of azimuthal angle φ , corresponding to $Q = 2 \text{ \AA}^{-1}$. (d) Difference scattering signal ΔS at $Q = 2 \text{ \AA}^{-1}$ versus P_2 (black dots) and straight line fit (red). The intercept with $P_2 = 0$ yields the isotropic scattering signal and the slope yields the anisotropic scattering signal, according to equation (11). The uncertainties ($\sigma_{\Delta S_0}$ and $\sigma_{\Delta S_2}$) are also estimated from the fit and further described in the text.

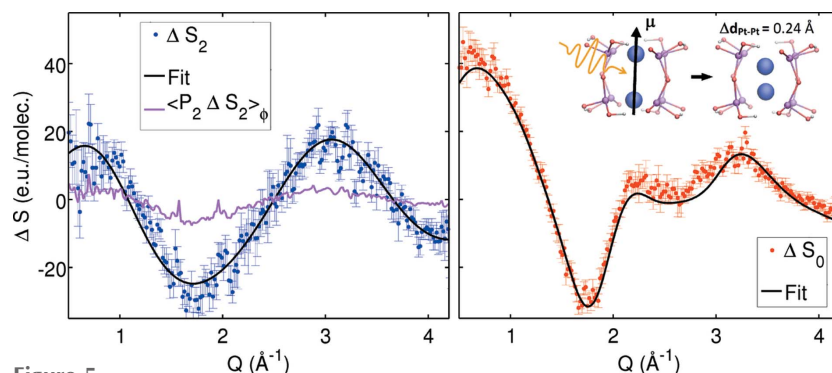


Figure 5
 ΔS_2 (left, blue points) and ΔS_0 (right, red points) extracted from the pattern in Fig. 4(b) through equation (11). The black line shows the simulated difference scattering signal through equations (9) and (10) using as parameters the best-fit results obtained by a combined fit of ΔS_2 and ΔS_0 . The magenta line in the left panel shows the azimuthal average of the anisotropic signal [$\langle -P_2(\cos \theta_Q) \Delta S_2 \rangle_\varphi$].

an average of 50 difference scattering patterns collected in a ~ 40 fs-wide time bin centred at 4.5 ps after the arrival of the laser pump pulse. As introduced above, such a signal arises mainly from the photoinduced contraction of the Pt atoms along their connecting vector. In the excited-state ensemble, this vector has a cosine-squared distribution with respect to the laser polarization axis, since the transition dipole moment is parallel to the Pt–Pt axis. Fig. 4(a) shows P_2 [$P_2 = (3 \cos^2 \theta_Q - 1)/2$ and $\cos \theta_Q$ as in equation (13)] mapped onto the CSPAD, with $\varphi = 0$ along the direction of the projection of the laser polarization axis on the detector surface, which was found to be inclined by 20° with respect to the vertical for the experiment described here.

For the analysis, the scattering pattern in Fig. 4(b) was divided into 500 radial bins and 45 azimuthal bins, and the signal in each bin was calculated as the average value of the pixels. The difference scattering signal corresponding to the radial bin centred at $Q = 2 \text{ \AA}^{-1}$ (black circle) is plotted in Fig. 4(d) as a function of $P_2(\cos \theta_Q)$ at the same Q value. The red line is a least-squares fit of a straight line to the data points. This fit, according to equation (11), yields ΔS_2 ($Q = 2 \text{ \AA}^{-1}$) as the slope and ΔS_0 ($Q = 2 \text{ \AA}^{-1}$) as the intercept with the $P_2 = 0$ axis. Repeating the procedure for all the radial bins yields the one-dimensional isotropic and anisotropic difference scattering curves for the full Q range at this specific time delay, as Fig. 5 shows.

3. Results and discussion

Fig. 5 shows the isotropic and anisotropic difference scattering signals extracted from the scattering pattern measured at 4.5 ps as a function of Q . The uncertainty estimates for ΔS_0 and ΔS_2 at each Q point are calculated from the covariance matrix of the coefficients of the straight-line fit. Since the difference scattering signal is usually of the order of 0.1–1% of the total scattering signal [see comparison between Fig. S1 of the supporting information and Fig. 4(b) for this experiment], averaging several difference scattering patterns acquired at the same nominal time delay allows the improvement of the

S/N ratio before the extraction of the isotropic and anisotropic contributions. Experimental parameters such as the magnitude of the differential scattering cross section and the X-ray photon flux, as well as the number of radial bins considered for each 2D pattern, determine the optimum number of images to be averaged for a specific experiment. The number of radial bins should be higher than the number of independent data points in the Q range [$\sim$ tens of points (Haldrup *et al.*, 2010)] and can be chosen arbitrarily high since re-binning can be done at a later stage of the analysis. For the present experiment, we set the number of radial bins to 500 and, for each time bin, we choose the number of images to be averaged by inspection of the decreasing uncertainties σ on the coefficients of the straight-line fit [ΔS_0 and ΔS_2 in equation (11)] as a function of number of averaged images. This is exemplified in Fig. 6(a) for the signal extracted at 4.5 ps: up to 50 averaged images, $\sigma_{\Delta S}$ decreases as the inverse square root of the number of averaged images, as expected for Gaussian noise; after 50 images, $\sigma_{\Delta S}$ converges to a constant value (~ 4 e.u. molec. $^{-1}$) since the noise is then dominated by systematic errors due to contributions from a non-constant background and the non-linear response of the detector rather than counting statistics (van Driel *et al.*, 2015). Therefore averaging more than 50 images will not further decrease the uncertainties on the measured signal.

Fig. 6(b) shows the number of unique P_2 values that are sampled for a specific Q value as a function of the number of azimuthal bins into which the 2D diffraction patterns is divided. The plot shows that choosing an odd number of azimuthal bins maximizes the number of unique points available for the fitting of ΔS versus P_2 . This behaviour arises from the dependency of P_2 on the azimuthal angle φ , as shown in Fig. 4(c), and from choosing equi-angular azimuthal bins. Moreover, since P_2 is non-linear as a function of φ , we introduce an error by calculating P_2 as the central value rather than the mean value in each azimuthal bin. This error can cause a significant decrease of the magnitude of the anisotropic difference scattering signal when decreasing the number of

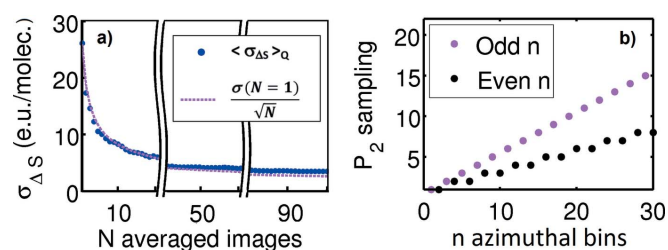


Figure 6

(a) Average of the uncertainties $\sigma(Q)$ on ΔS_2 over the full Q -range (500 radial bins) as a function of number of images averaged in the time bin centred at 4.5 ps. The uncertainties are estimated from the covariance matrix of the straight-line fit [equation (11)]. The dashed line shows that the magnitude of the uncertainties up to ~ 50 averaged images follows the behaviour of counting noise expected for a Gaussian distribution ($\sigma \propto N^{-1/2}$). (b) Number of different P_2 values that are sampled as a function of number of azimuthal bins. This parameter is maximized if the number of azimuthal bins is odd.

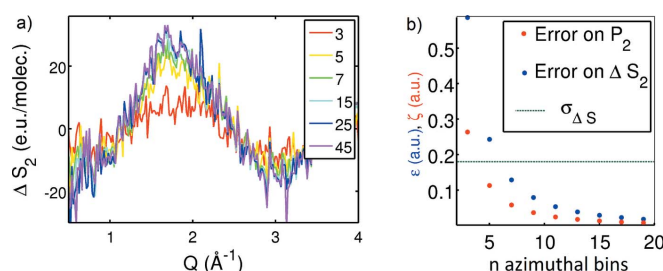


Figure 7

(a) Anisotropic difference scattering signals extracted from the 2D scattering patterns in Fig. 4(d) as a function of number of azimuthal bins. A significant decrease in the intensity of the signal is observed when decreasing the number of azimuthal bins below 5. (b) The red dots show the difference (ζ) between P_2 calculated as the central value in the azimuthal bins or as in equation (14): $\zeta = \langle P_2(\cos \theta_Q) \rangle_{2\delta\varphi} - P_2(\cos \theta_Q) = (3/4) \cos^2 \theta \cos 2\varphi [1 - (\sin 2\varphi / 2\delta\varphi)]$. With respect to this, the blue dots show the resulting difference (ϵ) in the magnitude of ΔS_2 (at $Q = 2$ Å $^{-1}$): $\epsilon = (\langle \Delta S_2 \rangle_{2\delta\varphi} - \Delta S_2) / \langle \Delta S_2 \rangle_{2\delta\varphi}$. The dashed black line shows the averaged experimental uncertainty $\sigma_{\Delta S_2}$ (divided by the measured signal).

azimuthal bins, as shown in Fig. 7(a). In order to calculate the mean value of P_2 , we should use the following expression,

$$\langle P_2(\cos \theta_Q) \rangle_{2\delta\varphi} = \frac{1}{2\delta\varphi} \int_{\varphi-\delta\varphi}^{\varphi+\delta\varphi} P_2(\cos \theta, \cos \varphi) d\varphi$$

$$= \frac{3}{4} \cos^2 \theta \left(1 - \frac{\sin 2\delta\varphi}{\delta\varphi} \cos 2\varphi \right) - \frac{1}{2}, \quad (14)$$

where $\delta\varphi$ is half the size of the azimuthal bins. Fig. 7(b) shows the difference between the values of P_2 (red dots) and of the magnitude of ΔS_2 (blue dots) obtained when calculating P_2 either as the central or the mean value of the azimuthal bins. From this observation, if the 2D scattering pattern is divided into more than five azimuthal bins, such a difference is within the uncertainty of the measurements ($\sigma_{\Delta S}$, the dashed green line) and can therefore be neglected, thus simplifying the calculations.

Since the isotropic difference scattering signal arises from the changes in the radial distribution functions (RDFs) of the sample (Dohn *et al.*, 2015), ΔS_0 in Fig. 5 comprises contributions arising from the changes in the structure of the solute and of the solvation shells, as well as from the changes in temperature and density of the bulk solvent (Haldrup *et al.*, 2010; Kjaer *et al.*, 2013; Ihse *et al.*, 2010; Cammarata *et al.*, 2006). The anisotropic scattering signal in Fig. 5 arises from the changes in the structure of the solute and potentially anisotropic changes in the solvation shell structure. The anisotropic response of the bulk solvent is discussed at the end of the section and, in the case of water, its contributions are negligible at time scales longer than a few hundred femtoseconds after excitation. In this experiment, the signal arising from the changes in the structure of the solute (ΔS^{solute}) is strongly dominated by the contraction of the Pt—Pt bond due to the very electron-rich Pt atoms. As Fig. S2 shows, in the limited Q -range available for this experiment, possible contributions to ΔS^{solute} arising from intramolecular changes

other than the Pt–Pt bond contraction are found within the uncertainties of the measured signal. Based on these considerations, we construct a modelling framework where the photoinduced structural changes in the structure of the solute are parametrized through a single structural parameter, $\Delta d_{\text{Pt-Pt}}$, which describes the changes in the Pt–Pt distance from the ground to the excited state of the molecule. Specifically, ΔS^{solute} is simulated from a set of structures derived by varying only the Pt–Pt distance of the density functional theory (DFT) optimized ground-state geometry of PtPOP. Details of the DFT calculations are provided in the supporting information. The full model used to fit the difference scattering signal measured at 4.5 ps after the photoexcitation of PtPOP is

$$\Delta S^{\text{model}}(Q, \Delta d_{\text{Pt-Pt}}) = \alpha \Delta S^{\text{solute}}(Q, \Delta d_{\text{Pt-Pt}}) + \beta \Delta S^{\text{cage}}(Q) + \Delta S^{\text{solvent}}(Q), \quad (15)$$

where the first term on the right-hand side is $\alpha_0 \Delta S_0^{\text{solute}}$, in the case of the isotropic signal, and $\alpha_2 \Delta S_2^{\text{solute}}$, in the case of the anisotropic signal. $\Delta S_0^{\text{solute}}$ and $\Delta S_2^{\text{solute}}$ are calculated using equations (9) and (10), respectively; α_0 and α_2 represent the fraction of excited-state molecules contributing to the isotropic and anisotropic scattering, respectively. ΔS^{cage} describes the changes in the structure of the solvation shells and β is a scaling factor. For the isotropic case, ΔS^{cage} was calculated from the RDFs of the solute–solvent atom pairs (Dohn *et al.*, 2015), as further described in the supporting information, while it was not necessary to include this term in the analysis of the anisotropic signal, given the good quality of the fit without the inclusion. Finally, $\Delta S^{\text{solvent}}$ describes the changes arising from the heating of the bulk water and its calculation is detailed in the supporting information. We note that, since the anisotropic signal is insensitive to the isotropic changes of the bulk solvent, fewer degrees of freedom are used in the description of the anisotropic data compared with the isotropic contribution. Equation (15) was fit to the measured difference scattering signal within a standard χ^2 minimization framework (Jun *et al.*, 2010). From a simultaneous fit of the isotropic and the anisotropic scattering signal, we find $\Delta d_{\text{Pt-Pt}} = 0.24 \pm 0.04 \text{ \AA}$, $\alpha_0 = 2.6 \pm 0.2\%$, $\alpha_2 = 1.5 \pm 0.2\%$. The black line in Fig. 5 shows the model constructed from the best-fit results, which well describe the data ($\chi^2 = 1.9$). $\Delta d_{\text{Pt-Pt}}$ is found in agreement with previous studies (Christensen *et al.*, 2009); the 1σ confidence interval on this parameter (0.04 Å) is found to be smaller than that obtained from fitting the isotropic and the anisotropic signals separately (which gives 1σ confidence intervals of 0.05 Å and 0.09 Å, respectively). Since changes in population fraction are not expected on these single-ps time scales (Gray *et al.*, 2017) and taking into account the decay of the anisotropic signal, as described below, we find that following the excitation event $\sim 2.6\%$ of the molecules have been photoexcited and contribute to the isotropic signal, and approximately 1.8 % contribute to the anisotropic scattering. We interpret this difference as an indication of multi-photon excitation of PtPOP, where the multi-photon excitation takes place through transitions

where the dipole moment is not parallel to the Pt–Pt axis (Stiegman *et al.*, 1987). This combined analysis may further allow the disentanglement of the contributions to the difference scattering signal arising from structural changes parallel or perpendicular with respect to the transition dipole moment. Specifically to PtPOP, the structural changes contributing to ΔS_2 depend directly on their displacement with respect to the Pt–Pt axis (ξ_{ij} in Fig. 3): equation (10) is maximum (and positive) when $\xi_{ij} = 0^\circ$ (*i.e.* when the structural change is displaced parallel to the Pt–Pt axis) and minimum (and negative) when $\xi_{ij} = 90^\circ$ (*i.e.* when the structural changes occur in the plane perpendicular to the Pt–Pt axis). However, as detailed above, the difference scattering signal is mainly dominated by the Pt–Pt contraction, and this hinders the investigation of additional structural parameters in the analysis described here.

The magenta line in Fig. 5 shows the signal obtained from an azimuthal integration of the anisotropic contribution re-projected onto the detector surface [$-P_2(\cos\theta_Q)\Delta S_2$] _{φ} . According to equation (11), this trace corresponds to the difference between the difference scattering signal obtained from an azimuthal integration of the 2D scattering pattern and the isotropic signal ($\langle \Delta S - \Delta S_0 \rangle_\varphi$). For the PtPOP data, such a difference is found to be $\sim 20\%$ of the magnitude of the isotropic contribution at time delays immediately after the excitation event, where the anisotropy is most pronounced. These observations show that the azimuthally integrated signal, at time scales shorter than the rotational correlation time of the solute, may not be a good approximation of the scattering arising from an isotropic ensemble of photoexcited molecules. This implies that at such time scales the use of azimuthally integrated scattering signals in subsequent analysis should be justified by comparing S_0 and azimuthally integrated signals.

Following the procedure described above, the anisotropic difference scattering signals were extracted from measured difference scattering patterns up to 1 µs after photoexcitation of PtPOP (see Movie S1). Fig. 8 shows the decay of the

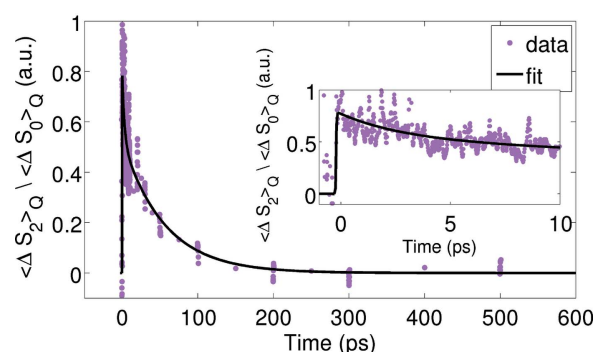


Figure 8 Ratio between the magnitudes (calculated as averages of the absolute values of the signal in the full Q -range) of the anisotropic and isotropic difference scattering signals as a function of pump–probe time-delay, up to 600 ps after the photoexcitation of PtPOP in water. A broadened bi-exponential decay is fit to the data (black line), with time constants of $3 \text{ ps} \pm 2 \text{ ps}$ and $60 \text{ ps} \pm 10 \text{ ps}$. The latter is interpreted as the rotational correlation time of PtPOP in water.

anisotropy as a function of increasing pump–probe time delay. We find that 20% of the anisotropic contribution to the signal decays with a time constant of $3 \text{ ps} \pm 2 \text{ ps}$; while 80% decays with a time constant of $60 \text{ ps} \pm 10 \text{ ps}$. The latter is interpreted as the rotational correlation time of the PtPOP molecule in water. Using the Stokes–Einstein–Debye model (Hornig *et al.*, 1997), the rotational correlation time of a sphere can be described as

$$\tau_r = \frac{4\pi\eta r^3}{3k_B T}, \quad (16)$$

where η is the viscosity of water, k_B is the Boltzmann constant, T is the temperature and r is the radius of the sphere. Approximating the PtPOP molecule to a sphere, and taking r as half the longest inter-atomic distance in the PtPOP molecule ($r = 4 \text{ Å}$), the rotational correlation time at room temperature can be estimated as 50 ps. This value is in agreement with the $\sim 60 \text{ ps}$ found in this analysis.

Finally, we note that the neat solvent may exhibit anisotropic scattering independently of the photoexcited solute molecules: the laser pulse weakly perturbs the equilibrium structure of the solvent through non-resonant excitations predominantly aligned with the polarization of the laser, and the X-ray pulse probes the induced structural dynamics. Optically, the sample becomes birefringent, with different indices of refraction for light polarized parallel or perpendicular to the laser polarization axis. From an X-ray point of view, the scattering patterns are observed to be anisotropic and the analysis described above can be applied to extract the anisotropic scattering as a function of Q and time delay. The time evolution of the anisotropic X-ray scattering signal can be directly compared with the impulsive nuclear-coordinate response measured through techniques such as Raman-induced Kerr effect spectroscopy (Palese *et al.*, 1994; Castner *et al.*, 1995). Since the time scales of this nuclear response are known from optical Kerr effect studies, the anisotropic solvent scattering signal can be used to estimate the time-zero (the arrival time of the laser pulse at the sample) and the instrument response function (IRF) of the experiment (Biasin *et al.*, 2016). The separate determination of these parameters significantly improves the analysis of the isotropic part of the scattering signal, by reducing the number of free parameters in the model used to fit the data (Biasin *et al.*, 2016). This method of extracting the IRF and time-zero can be used as a diagnostic for any time-resolved XDS experiment on solvated molecules where the anisotropic solvent response can be clearly identified.

4. Conclusions

In summary, the formalism introduced by Baskin & Zewail (2006) and expanded by Lorenz *et al.* (2010) has been applied here to separate isotropic and anisotropic contributions from 2D difference scattering patterns measured upon photoexcitation of the solvated PtPOP molecule at an XFEL. The presented formalism has been directly implemented in quantitative structural analysis and we find that a combined

analysis of the isotropic and anisotropic difference scattering signals helps the disentanglement of the many degrees of freedom involved in the structural response of the sample to photoexcitation and enhances the structural sensitivity. This analysis approach is generally applicable for all molecular systems with a well defined transition dipole moment and asymmetric structural response to photoexcitation, provided a time-resolution shorter than the rotational dephasing time. Furthermore, we have discussed how the quantitative analysis of the anisotropic scattering signal can provide access to anisotropic solvent dynamics induced by the linearly polarized pump pulse and how these measurements can lead to independent determination of time-zero and the IRF of the experiment. In conclusion, we have demonstrated a method that allows quantitative interpretation of anisotropic scattering signals measured at XFELs from aligned ensembles of molecules. The information delivered by this method can benefit the overall interpretation of high-content scattering data from solution-state molecular systems.

5. Related literature

The following references, not cited in the main body of the paper, have been cited in the supporting information: Bahn & Jacobsen (2002); Becke (1988); Che *et al.* (1983); Dohn *et al.* (2017); Enkovaara *et al.* (2010); Himmetoglu *et al.* (2012); Larsen *et al.* (2009, 2017); Lee *et al.* (1988); Maurer & Reuter (2011); Mortensen *et al.* (2005); Ozawa *et al.* (2003); Pinto *et al.* (1980); Sørensen & Kjaer (2013); Yasuda *et al.* (2004); Ziegler *et al.* (1977).

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Paper III

Solvent Manipulation of Charge Transfer Excited State Relaxation Pathways in $[\text{Fe}(\text{2,2'}\text{-bipyridine})(\text{CN})_4]^{2-}$

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Solvent control of charge transfer excited state relaxation pathways in $[\text{Fe}(2,2'\text{-bipyridine})(\text{CN})_4]^{2-}$

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The excited state dynamics of solvated $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$, where bpy = 2,2'-bipyridine, show significant sensitivity to the solvent Lewis acidity. Using a combination of optical absorption and X-ray emission transient spectroscopies, we have previously shown that the metal to ligand charge transfer (MLCT) excited state of $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ has a 19 picosecond lifetime and no discernable contribution from metal centered (MC) states in weak Lewis acid solvents, such as dimethyl sulfoxide and acetonitrile.^{1,2} In the present work, we use the same combination of spectroscopic techniques to measure the MLCT excited state relaxation dynamics of $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ in water, a strong Lewis acid solvent. The charge-transfer excited state is now found to decay in less than 100 femtoseconds, forming a quasi-stable metal centered excited state with a 13 picosecond lifetime. We find that this MC excited state has triplet (³MC) character, unlike other reported six-coordinate Fe(II)-centered coordination compounds, which form MC quintet (⁵MC) states. The solvent dependent changes in excited state non-radiative relaxation for $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ allows us to infer the influence of the solvent on the electronic structure of the complex. Furthermore, the robust characterization of the dynamics and optical spectral signatures of the isolated ³MC intermediate provides a strong foundation for identifying ³MC intermediates in the electronic excited state relaxation mechanisms of similar Fe-centered systems being developed for solar applications.

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Introduction

Inorganic complexes are attractive candidates for solar energy applications due to their tunable electronic properties, which

can be varied synthetically by changing the metal atom and ligand composition or structure. Molecular photosensitizers based on 4d and 5d transition metals, such as Ru and Ir, have been successfully implemented in photovoltaic applications

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due to their intense absorption, long-lived charge transfer excited states, and their ability to undergo reversible redox processes.³ However, their cost and scarcity render them impractical for large-scale development.

Transferring the functionality of 4d and 5d transition metal complexes to the more abundant 3d transition metal centered systems motivates wide-ranging investigations targeting solar energy applications.⁴ Solar energy applications benefit from long-lived metal-to-ligand charge-transfer (MLCT) excited states, but the majority of optically generated MLCT excited states in 3d transition metal complexes relax on the sub-ps timescale. A central challenge to extending the charge transfer excited state lifetimes in light harvesting complexes based on 3d transition metals is the weaker ligand field splitting of 3d complexes, relative to their 4d or 5d counterparts. The smaller ligand field splitting leads to ligand field excited states with lower energies than the optically bright charge transfer excited states that very efficiently quench the MLCT excited states. This deactivation reduces the MLCT lifetime of 3d transition metal complexes by orders of magnitude compared to their 4d and 5d analogs. For instance, ruthenium(II)-centered polypyridyl compounds are characterized by MLCT states with hundreds of nanoseconds to microseconds lifetimes,^{5–9} the MLCT state of similar complexes with an isoelectronic iron(II) center undergoes spin crossover to a metal centered quintet (⁵MC) state within hundreds of femtoseconds.^{10–24}

Significant progress in the design of iron-centered molecular systems with extended MLCT lifetimes targeted at solar energy applications has been made recently and demonstrates the potential of suppressing internal conversion and intersystem crossing.^{2,25–30} The synthetic strategy pursued with the most success for octahedral iron(II) complexes has been ligand selection for increased ligand-to-metal σ -donation, beyond that of typical polypyridyl ligands. Increased σ -donation leads to larger ligand field splitting and destabilization of the MC excited states relative to MLCT excited states. A range of strong σ donating N-heterocyclic carbene ligands have provided Fe-complexes with MLCT lifetimes ranging from ~ 300 fs to ~ 30 ps,^{2,25,27,30,31} long enough to allow transfer of the ligand-localized electron for photovoltaic applications.^{27,28}

The metal centered triplet (³MC) excited state has recently been suggested to play a critical role in mediating the MLCT decay pathway in the cases of both Fe(II)-centered spin crossover complexes (short-lived, ~ 100 fs, MLCT states)^{21,22} and MLCT complexes (long-lived, ~ 20 ps, MLCT states),^{2,26,29,30} and has additionally been observed as a precursor for ligand dissociation following excitation of $[\text{Fe}(\text{CN})_6]$.^{4–32} Although still under debate,¹⁸ much experimental and computational evidence supports the presence of a very short lived ³MC transient state in the spin state transition dynamics to the relatively long lived ⁵MC state.^{20–22,33,34} In the cases where MLCT lifetimes are extended to the picosecond time scale, they decay without well characterized intermediates, thus preventing experimental identification of decay-mediating states. Quantum chemical and dynamics calculations for several such complexes do suggest that the MLCT lifetime is strongly influenced by the

relative positions of the potential curves of the MLCT and ³MC excited states.^{2,26,29,35–38} Although the important role of the ³MC state in facilitating the excited state decay of hexa-coordinated Fe(II) complexes has been suggested, a metastable ³MC state has yet to be cleanly isolated for these complexes. Therefore, it is difficult to assess the capacity of experimental methods to identify the role of ³MC intermediates in the excited state dynamics of Fe-based systems.

A strong solvatochromic effect has been well-established for Fe- and Ru-centered cyano-polypyridyl complexes,^{39–44} and has been ascribed to the interaction of high Lewis acidity solvents (such as water) with the N lone pair of the CN^- ligand. Here, we exploit the solvent-dependent electronic structure of $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$, illustrated in Fig. 1, to vary the relative energies of the MLCT and MC states with the intent of generating a metastable ³MC. The choice of $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ was motivated by previous transient optical measurements that demonstrate the loss of characteristic MLCT features from the excited state spectrum upon changing the solvent Lewis acidity.⁴⁵ This study clearly demonstrated the solvent dependence of the non-radiative relaxation in this complex, but did not have the time resolution to determine relaxation rates nor the ability to determine the MC excited state intermediate formed in water.⁴⁵ The use of such a chemically amenable system allows us to develop our current understanding of how metal–ligand bonding controls the internal conversion and intersystem crossing pathways in 3d transition metal complexes. In this regard, the solvatochromic $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ mixed ligand complex provides an excellent model for addressing these fundamental questions in physical chemistry, as the degree of metal–ligand σ - and π -bonding interactions can be varied with the solvent. Steady-state measurements have shown this interaction to shift electron density on the cyanide ligand and increase the metal-to-ligand π

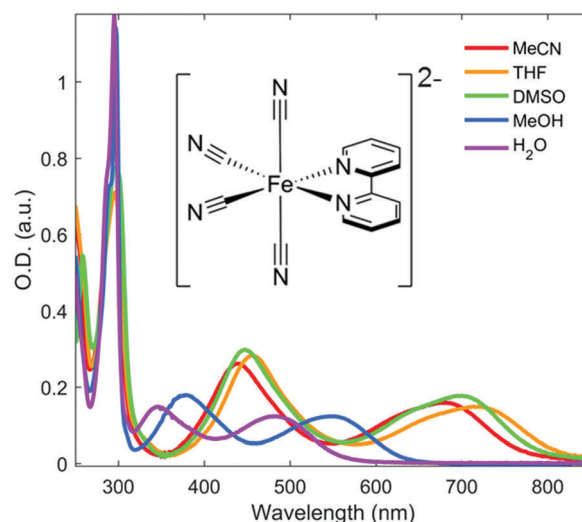


Fig. 1 Solvatochromism of $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$. The inset shows the $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ system, and the rest of the panel shows its optical absorption spectrum in a series of solvents with varying Lewis acidity: acetonitrile (MeCN) tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), methanol (MeOH), and water (H_2O).

back-donation for the water-solvated complex.^{39,40,46} The highest occupied molecular orbitals (HOMO) of mixed Fe d (t_{2g}) and cyano π^* character are therefore stabilized relative to the lowest unoccupied molecular orbitals (LUMO) of bpy-ligand π^* character, resulting in a net destabilization of the respective MLCT excited state.⁴⁷ Experimental investigation of the solvent influence on the MC levels is significantly more scarce, but one study finds the trend of solvent-dependent excited state lifetimes for Ru cyanopolypyridyl complexes can be qualitatively reproduced under the assumption that the MC energy levels are unchanged relative to the ground state.⁴⁴

To characterize the excited state dynamics of $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ in water we have combined UV-visible pump-probe spectroscopy measuring the transient optical absorption (TA) with transient K-edge X-ray emission spectroscopy (XES), a combination which have delivered key insights in the dynamics of 3d transition metal centered systems before.^{1,21,48–52} The signal recorded by TA arises from dipole-allowed transitions in the optical regime, rendering it sensitive to charge transfer excited states involving ligand-localized excited electrons. XES monitors the fluorescence emitted during the 2p-to-1s or 3p-to-1s decay following 1s core-hole ionization of the Fe metal center. The fluorescence intensity and spectral features are sensitive to the total spin moment on the iron center, and therefore, this method can distinguish MC excited states differing in Fe spin moments, such as ^3MC and ^5MC states. The combination of the two techniques enables full characterization of the excited state relaxation pathway of 3d transition metal complexes. The present study has unambiguously identified a metastable ^3MC excited state with the transient XES spectrum. This identification, in combination with the TA measurements enables the assignment of transient absorption features in the UV-visible spectrum to the ^3MC excited state that should prove valuable to the interpretation of electronic excited state relaxation dynamics in other Fe(II) systems.

We report the excited state dynamics of $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ solvated in water and identify a temporally isolated ^3MC intermediate for the first time. In contrast, we have previously demonstrated a long lived MLCT excited state (19 ps) for $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ in weak Lewis acidic solvents (dimethyl sulfoxide (DMSO) and acetonitrile (MeCN)), with no discernable contribution from metal centered states.¹ In the present work, we shift the bpy-localized MLCT state towards higher energy by using a high Lewis acidity solvent results in a faster MLCT-to-MC transition and slower MC-to-GS transition. The identification of a metastable ^3MC state provides further support for its role in deactivating MLCT excited states in Fe(II) complexes, and expands on the previously reported studies on Ru-centered systems which were unable to distinguish the influence of the solvent on the MC state energy levels.⁴⁴

Experimental methods

X-ray emission

The time-resolved XES measurements were conducted at the X-ray Pump-Probe (XPP)⁵³ end station at the Linac Coherent

Light Source (LCLS). An aqueous solution of 55 mM $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ was pumped through a 50 μm diameter nozzle producing a cylindrical liquid jet. The sample was excited with 400 nm optical laser pulses of 45 fs duration, 120 μm focus diameter (FWHM), and 12.5 μJ per pulse, delivering a pulse fluence of $3 \times 10^{12} \text{ W cm}^{-2}$. The sample was probed by 8.5 keV X-ray laser pulses of ~ 30 fs duration. The Fe 3p-1s ($\text{K}\beta$) fluorescence XES signal was detected on a 140k Cornell-SLAC Pixel Array Detector (CSPAD) area detector⁵⁴ located above the liquid jet using four dispersive Ge(620) crystal analyzers with a central Bragg angle of 79.1 degrees.⁵⁵ The Fe 2p-1s ($\text{K}\alpha$) fluorescence XES signal was detected on a second 140k CSPAD detector placed behind the sample, using a spherically bent Ge(440) crystal analyzer, set to a Bragg angle corresponding to the maximum signal of the iron $\text{K}\alpha$ fluorescence of 6404 eV (75.4 degrees).

The full 2D images of the XES detectors were read out for each pump-probe event, normalized, and corrected as described in the ESI.† Difference images were constructed by subtracting a reference signal recorded from optical laser-off probe events for every seventh X-ray laser pulse event throughout the data collection. The difference images of each pump-probe event were then sorted into 250 individual time bins (400 shots per bin) according to their individually recorded time delay (see the ESI,† for a description of the timing tool diagnostic). The $\text{K}\alpha$ difference images for each time bin were averaged and integrated, resulting in the kinetic trace presented in Fig. 5, while the $\text{K}\beta$ difference images of each time bin were averaged and integrated along the nondispersive detector axis, resulting in the difference spectra presented in Fig. 6A.

The static $\text{K}\alpha$ XES spectra of reference compounds were measured at the Stanford Synchrotron Radiation Lightsource (SSRL) beamline 6-2. Reference compounds were obtained from Sigma-Aldrich and used as-is. Samples were measured as powders (covered by Kapton tape) in a cryostat at 10 K. Samples were excited with monochromatic incident X-rays at 7300 eV (double-crystal Si(311) monochromator, 0.2 eV FWHM bandwidth) and Fe $\text{K}\alpha$ fluorescence was detected with a Rowland geometry spectrometer utilizing (440) Bragg reflection from bent Ge crystals with a 1 m radius of curvature (energy resolution 0.6 eV FWHM).⁵⁶ X-rays were detected with a Si drift detector and a correction for detector nonlinearity was applied. The monochromator energy was calibrated with an Fe foil and the spectrometer calibration and transmission correction was done using elastic scattering. Each sample was checked for X-ray induced damage by measuring the Fe X-ray absorption near-edge structure (XANES) spectra at various incident fluxes using filters installed in the beamline. Each sample was measured multiple times at different positions to reduce exposure.

Optical transient absorption

Femtosecond time-resolved UV-visible transient absorption (TA) measurements were conducted on $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ samples in H_2O (7 mM) and DMSO (2 mM), prepared directly before the experiments. Liquid sheet jets with 100 μm and 200 μm thicknesses were used to deliver the sample into the pump-probe overlap region, respectively. Continuous flow of the jet

ensured that any accumulation of photo-damaged sample was avoided.

Experiments were carried out using an amplified Ti:sapphire laser system (Coherent Mantis with Coherent Legend Elite Duo) with a 5 kHz repetition rate, 800 nm central wavelength, 2 mJ pulse energy and 40 fs FWHM pulse duration. A portion of the laser pumped an optical parametric amplifier (Spectra-Physics OPA-800C) to generate near IR signal and idler *via* difference frequency mixing. The output of the OPA was used to generate 500 nm pump pulses *via* sum-frequency generation of the signal with 800 nm light, and to generate 700 nm pump pulses *via* frequency doubling of the signal in a BBO crystal. The pump pulse was directed to the sample through a delay stage, a 2.5 kHz chopper, and a lens, resulting in pump pulses with 100 μm focus diameter (FWHM), 50 fs duration, and 1.6 μJ pulse energy providing a pump fluence of $4 \times 10^{11} \text{ W cm}^{-2}$. The pump was overlapped with a white light probe pulse (*via* supercontinuum generation in 4 mm of CaF_2) at the sample position. The probe was transmitted through the sample and imaged on a spectrometer (Horiba Jobin Yvon iHR320, grating 150 grooves per mm). The probe spectrum was recorded at 5 kHz with a NMOS linear image sensor (Hamamatsu, S8380-512Q) simultaneously over the whole 300–700 nm spectral range. The differential absorbance (ΔA) was calculated as $\Delta A = \log(I_{\text{off}}/I_{\text{on}})$, where I_{on} and I_{off} are the pumped and unpumped intensity, respectively. Overall time-resolution of the experiment was approximately 100 fs.

Results and discussion

Steady-state and transient optical absorption spectroscopy

The steady-state optical absorption spectrum of $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ in a series of solvents is presented in Fig. 1. In weak Lewis acid solvents (acetonitrile (MeCN, red), tetrahydrofuran (THF, orange), and dimethyl sulfoxide (DMSO, green)) the visible spectrum is

characterized by two absorption features at roughly 450 nm and 700 nm assigned to MLCT excitations from orbitals of mixed Fe d and cyano π and π^* character to π^* orbitals of the bipyridine ligand.⁵⁷ For high Lewis acidity solvents, such as the hydrogen-bonding methanol (MeOH, blue) and H_2O (purple), these absorption features blue-shift. This solvatochromic effect has been extensively mapped for cyano-polypyridyl Fe and Ru complexes and shown to be linear, both with respect to the solvent acceptor number (a measure of the Lewis acidity) and the number of cyano ligands present.^{39,40,42,57} This makes $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ in solution an archetypical system to characterize the influence of the solvent Lewis acidity on the properties of these complexes.

The blue-shift of the MLCT absorption band clearly shows that increasing solvent Lewis acidity strongly destabilizes the MLCT state with respect to the ground state. To investigate how the solvent influences the energy levels of the MC states, and to determine how this modifies the MLCT deactivation pathways, we turn to the solvent dependence of the excited state relaxation dynamics.

Fig. 2 shows the solvent-dependent differential absorption spectra of $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ obtained after excitation of the lowest energy MLCT transition (700 nm in DMSO, 500 nm in water). In DMSO (Fig. 2A), the differential spectra at all time delays are characterized by the ground state bleach (GSB), overlaid with a broad excited state absorption (ESA) feature everywhere below 600 nm, peaking at 370 nm and 525 nm. In bipyridine-containing complexes, the strong 370 nm ESA feature is typically associated with an excited electronic state having an electron localized on the pyridyl ligand.^{1,2,23,58,59} In previous work, we have complemented such TA measurements by K β XES, determining that the excited state dynamics are well-described by a 19 ps single-exponential decay of a bipyridine-localized MLCT state.¹ In water (Fig. 2B), the difference spectra at very early time delays (~ 100 fs) can also be described by the GSB overlaid by a similar ESA feature everywhere below

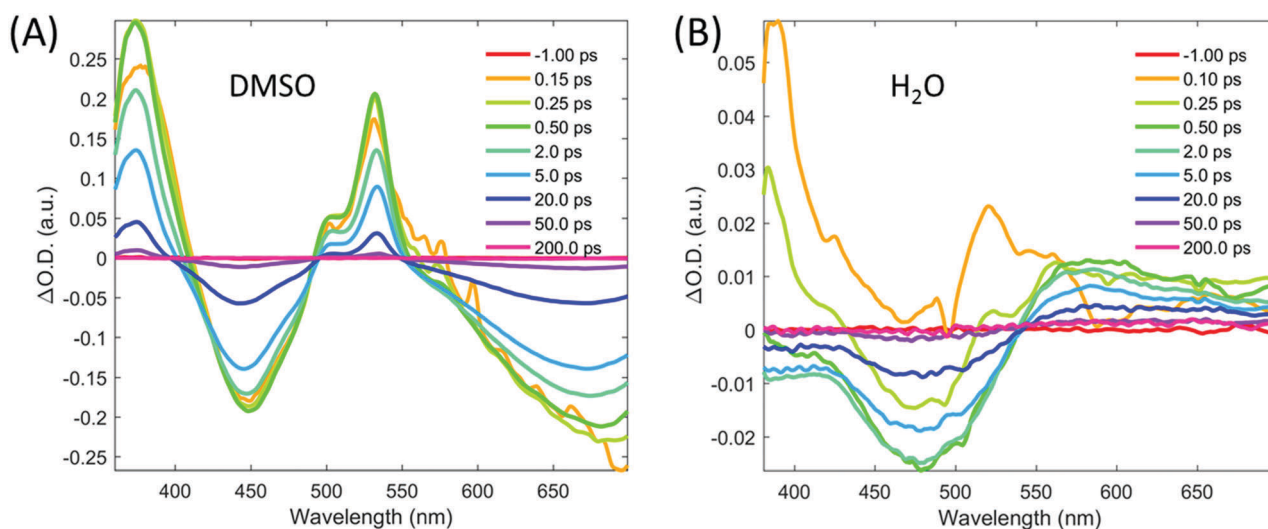


Fig. 2 Transient absorption spectra of $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ at selected time delays in (A) DMSO with 700 nm excitation and (B) water with 500 nm excitation.

600 nm, peaking at 370 nm and 525 nm. However, within half a picosecond, the initial ESA features decay completely. Differential spectra at time delays longer than 0.5 ps are characterized by the GSB and a broad ESA feature above 600 nm. These features decay together over the following 50 ps as the ground state spectrum recovers. For $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ in water, the ultrafast appearance and decay of the 370 nm ESA feature without the decay of the ground state bleach indicates that the excitation of the MLCT band initially populates a very short-lived bipyridine-localized MLCT state, which decays to a secondary electronic excited state before returning to the ground state on the tens of picosecond time scale. As described in the ESI,[†] high excitation fluencies lead to a longer lived absorption feature centered at 680 nm characteristic of the solvated electron⁶⁰ arising from multiphoton ionization.

From the optical data presented in Fig. 2B, the excited state cascade in aqueous solution can be formulated as an instantaneous generation of an MLCT state and a small fraction (<0.01) of photoionization products. The MLCT state undergoes ultrafast conversion to a second excited state which decays on the picosecond timescale, while the photoionization product remains. When this three-state model is implemented in a global analysis framework and applied to the data, the species associated spectra (SAS) shown in Fig. 3 are identified. SAS1, which we associate with the MLCT state, decays with a 0.17 ± 0.03 ps lifetime. SAS2, which we associate with the second excited electronic state, decays with a lifetime of 12.7 ± 0.4 ps. SAS3, which we associate with the solvated electrons remains within the 1 ns time window of these measurements.

To facilitate the direct comparison of the excited state dynamics measured with TA at low fluence to those measured by XES at higher fluence, we have applied the same analysis to additional TA measurements recorded at higher fluence, which exhibit a significant contribution from solvated electrons. The transient spectra and resulting SAS are shown in the ESI.[†]

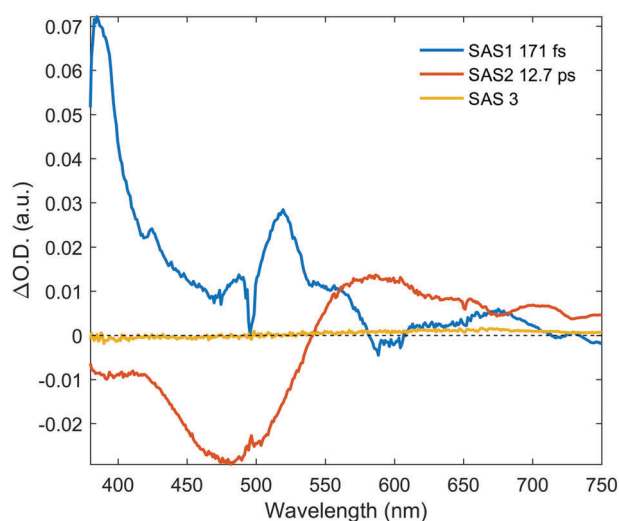


Fig. 3 Species associated spectra (SAS) from a global analysis of the transient absorption data for $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ dissolved in water and shown in Fig. 2B.

The spectral features of the photoexcited states (SAS1 and SAS2) are virtually identical between the high and the low fluence measurements, and the variation in the extracted relaxation dynamics lies within the uncertainties of the measurements. This demonstrates that the decay pathway of the single-photon MLCT non-radiative relaxation is independent of the excitation conditions over a large range of pump fluence.

Assigning the nature of the second electronic excited state associated with SAS2 in the global analysis is difficult based on optical TA data alone. The broad and relatively weak >600 nm ESA is the only significant spectral feature outside the ground state bleach. This ESA lacks significant or defining features that might otherwise allow assignment of the associated species. The short lifetime and complete ground state recovery rules out ionization and degradation products as candidates for SAS2. The lack of low-lying unoccupied ligand-centered electronic states (other than the bipyridine π^* states) suggests that SAS2 describes a secondary excited state with MC character. To unambiguously determine the nature of this intermediate, we turn to the transient $K\alpha$ and $K\beta$ XES measured at the LCLS X-ray free-electron laser.

Transient X-ray emission spectroscopy

$K\alpha$ and $K\beta$ XES monitors the 2p-to-1s and 3p-to-1s fluorescence, respectively, following 1s core-hole X-ray ionization. The strong influence of the exchange interaction between the np and the 3d valence electrons make the XES spectra sensitive to the total spin multiplicity on the iron center.^{56,61–64} The spin-sensitivity of the two techniques is illustrated by the reference spectra shown in Fig. 4A and B. The reference spectra are measured for a series of Fe-centered compounds with ground state electronic structure similar to those of the potential excited states of $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$. By selecting reference compounds with ligand bond covalency similar to $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$, good agreement between the reference spectra and the measured data is expected. By subtracting the reference signal of the ground state compound, from the references for the potential excited states, the reference difference spectra, illustrated in Fig. 4C and D can be constructed.

The $K\beta$ spectra exhibit the clearest spectral shape variation between different electronic states, such that direct comparison between transient $K\beta$ data and reference difference spectra allows for robust identification of the excited electronic states. Meanwhile, the $K\alpha$ emission is roughly an order of magnitude more intense than the $K\beta$ emission, which makes the $K\alpha$ data well suited to derive the time scales of the underlying relaxation dynamics. Based on these considerations, we have measured $K\alpha$ single-energy kinetics to determine the characteristic time scales of the experiment (time-zero, instrument-response function (IRF), and lifetimes), and measured full $K\beta$ transient spectra for robust excited state identification. Since the $K\alpha$ and $K\beta$ data were recorded simultaneously, the time zero, temporal resolution, and quantum yields of the two datasets are identical. Therefore, the characteristic time constants of the experimental parameters, as well as the excited state lifetimes, determined from the high signal-to-noise $K\alpha$ kinetic data can be used in a global analysis framework for the $K\beta$ spectral data.

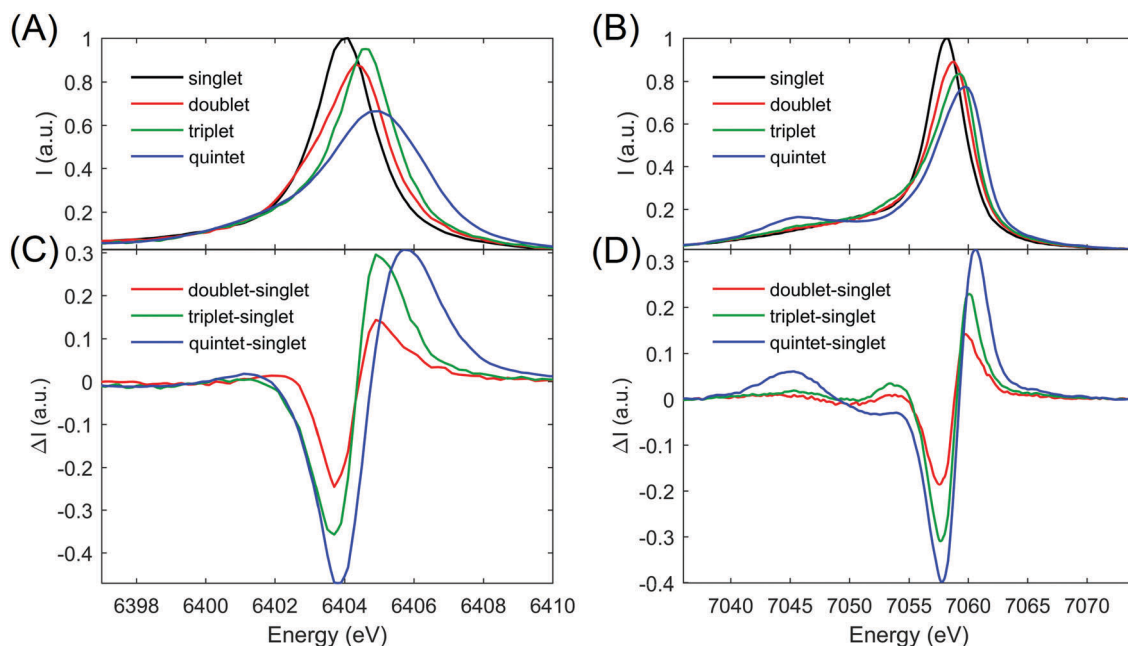


Fig. 4 $K\alpha$ (A) and $K\beta$ (B) reference spectra measured for a series of Fe model complexes of similar spin state configuration as the potential excited states in this study. $K\alpha$ references are $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ (singlet), $[\text{Fe}(\text{CN})_6]^{3-}$ (doublet), $\text{Fe}(\text{phthalocyanine})$ (triplet), and $[\text{Fe}(1,10\text{-phenanthroline})_2(\text{NCS})_2]$ (quintet). $K\beta$ references are taken from Zhang *et al.*¹ Reference difference spectra (C and D) constructed from the $K\alpha$ and $K\beta$ references generated by subtracting the ground state reference from each of the excited state references.

The $K\alpha$ kinetics shown in Fig. 5 were recorded at 6404 eV. As reported elsewhere,⁶² and seen from the reference difference spectra (Fig. 4C), the $K\alpha$ difference intensity at 6404 eV allow us to monitor the total spin increase on the Fe center. We observe that the growth of the transient signal is delayed with respect to a broadened Heaviside step function. This delay arises from an

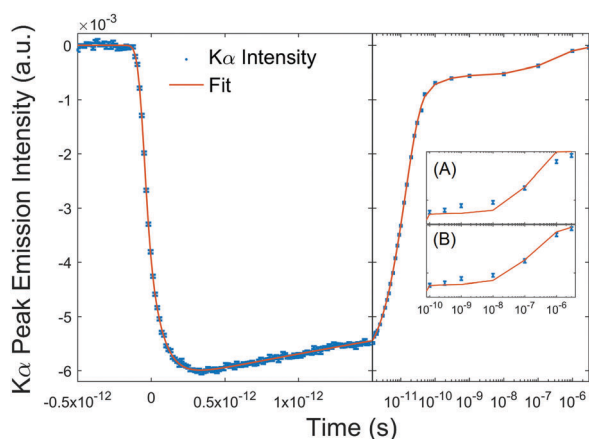


Fig. 5 Kinetics of the $K\alpha$ peak emission intensity measured at 6404 eV following MLCT excitation of $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ in water. Blue data points are binned in 10 fs steps and supplied with error bars indicating the standard error. The red curve shows the fit of the data as described in the main text. Insets (A) and (B) show fits to the late data points using first and second order reaction kinetics, respectively. The second order reaction kinetics (B), capture the evolution of the data better, illustrating that the kinetics are due to charge-recombination of photoionized $[\text{Fe}(\text{bpy})(\text{CN})_4]^-$ with solvated electrons, as described in detail in the ESI.†

excited state relaxation that results in a secondary increase in the Fe spin-moment, delayed with respect to excitation of the MLCT state. Overall, the growth is best described by the sum of a Heaviside step function and exponential grow-in broadened by a Gaussian representing the instrument-response function. The step function accounts for the instantaneously populated $^1\text{MLCT}$ and photoionization products.^{65,66} These species each have a single unpaired electron on the Fe center, making them formal doublets with respect to the Fe center, and therefore they cannot be distinguished with the XES data. The exponential growth accounts for the transition from the MLCT to the secondary excited state of higher spin-moment. The fact that the Fe spin-moment increases for the secondary excited state confirms the assumption, based on the optical TA data, that the decay of the MLCT state leads to the population of an MC state with higher spin. The decay of the transient $K\alpha$ signal is dominated by the single-exponential lifetime of the secondary MC excited state, but also includes a weaker long time-scale component for the recovery of the photoionization products.

In fitting the data to the kinetic model described above, a time-zero and IRF (rms) of -54 ± 4 fs and 34 ± 2 fs are recovered, with the uncertainty reflecting the standard deviation. The exponential component of the growth accounts for a $40 \pm 4\%$ increase of the total signal and has a time constant of 87 ± 5 fs, which we assign to the MLCT-to-MC transition. The decay is dominated by a component with a 13.1 ± 0.4 ps lifetime, readily assigned to the decay of the MC state and recovery of the ground state accounting for 84% of the decay. The remaining decay of the transient signal occurs on the hundreds-of-nanoseconds to microsecond time scale. The MLCT-to-MC

transition observed by the XES is faster than the lifetime associated with SAS1 in the TA analysis. This discrepancy likely reflects the challenge of differentiating intramolecular vibrational relaxation and population decay in TA, combined with the challenges of properly subtracting out cross-phase modulation artefacts.

The long time scale dynamics of the ground state recovery matches the expected second-order kinetics (as described in the ESI†) for the recovery from the photoionized $[\text{Fe}(\text{bpy})(\text{CN})_4]^-$.⁶⁰ Comparative fits to the long time delay data using first- and second order rate expressions for the decay are illustrated in Fig. 5 as insets (A) and (B), respectively. A detailed discussion of the mechanism and time scale of the recovery can be found in the ESI.† The increased ratio of photoionization product (16%) compared to the TA data is due to the increased laser power used for the XES experiments.

In summary, the $\text{K}\alpha$ decay kinetics can be described by the same model used to interpret the TA data. Since the TA experiment shows that the dynamics of the single-photon excited state pathway is independent on the amount of two-photon excitation, the XES data can be used to identify the spin state of the 13 ps MC intermediate associated with SAS2 in the TA analysis. For this excited state identification, we rely on the $\text{K}\beta$ data recorded simultaneously with the $\text{K}\alpha$ data.

Transient $\text{K}\beta$ differential spectra measured at multiple time delays are presented in Fig. 6A. Qualitative comparison of the data recorded at 0.5–5 ps (delays dominated by the MC intermediate) with the reference spectra in Fig. 4D reveals that the $\text{K}\beta'$ shoulder at 7045 eV is very weak. This allows the high spin ^5MC state to be eliminated as the dominant product of the MLCT decay and makes a ^3MC the most likely candidate for the MC excited state. To explicitly identify the nature of the MC state and derive excitation and speciation fractions, we have conducted a global analysis of the transient $\text{K}\beta$ data using a three-state model that includes the MLCT state, the MC state,

and the $[\text{Fe}(\text{bpy})(\text{CN})_4]^-$ photoproduct. Using the excited state cascade and time scales from the $\text{K}\alpha$ analysis, the species associated spectra (SAS) for the excited states were extracted.

The extracted SAS are shown in Fig. 6B. SAS1 describes the signal that is lost with the 85 fs time constant after the excitation. SAS2 describes the signal that grows in as SAS1 decays, and has a lifetime of 13.1 ps. SAS1 was definitively identified as an MLCT state from the optical TA, and could therefore be used to establish a scaling factor between the SAS and reference difference spectra by minimizing the chi-squared between SAS1 and the MLCT (doublet–singlet) reference difference signal. Upon establishing this scaling factor, a quantitative comparison of SAS2 (representing the MC excited state) can be made against the triplet and quintet reference difference spectra (all plotted in Fig. 6B). It is immediately apparent that the signal shape, and in particular signal amplitude, of SAS2 matches the reference spectrum obtained for the ^3MC state. Taken together with the lack of additional fast time constants in the excited state cascade, the agreement between SAS2 and the ^3MC reference difference spectrum definitively assigns the ultrafast interconversion observed in the optical TA and $\text{K}\alpha$ data to an MLCT-to- ^3MC interconversion. Furthermore, the spectral features of SAS2 in the optical TA analysis can now be assigned as characteristic of the ^3MC state. The ultrafast XES measurements provide a robust assignment of the ^3MC state, which enables the interpretation of the ESA seen in the optical pump–probe measurement. The most significant feature of the spectrum is the excited state absorption feature at 570 nm, to the red side of the ground state bleach. Similar, but somewhat weaker, ESA features have been observed for ^3MC states assigned of Ru-centered polypyridyl complexes.⁶⁷

Solvent-dependent electronic structure

The solvent Lewis acidity strongly influences the excited state dynamics of $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$. Increasing solvent Lewis acidity

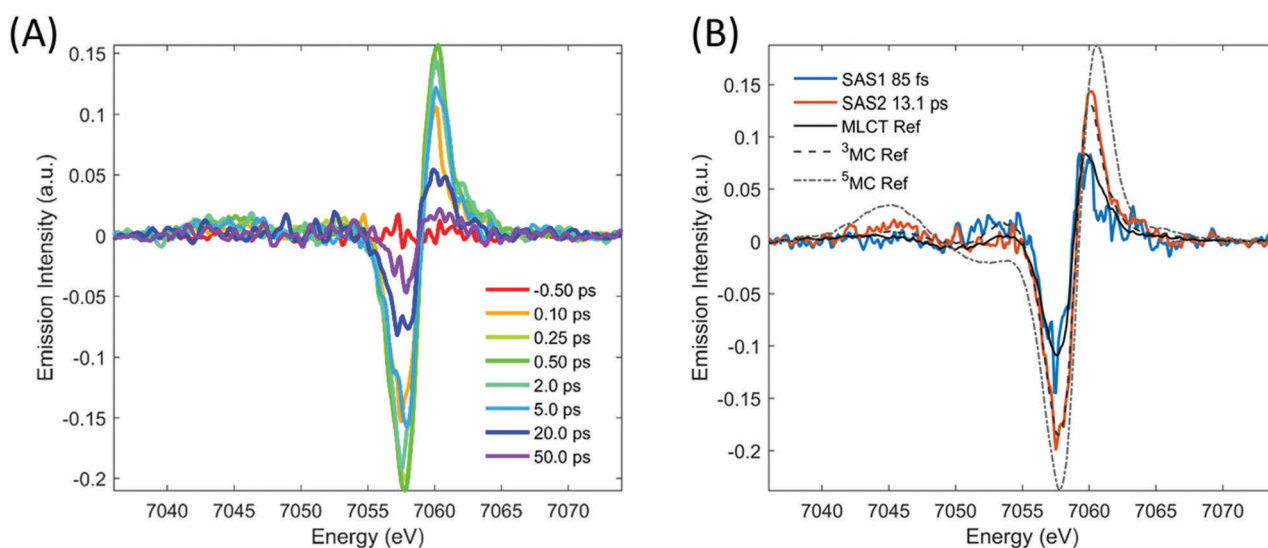


Fig. 6 Transient $\text{K}\beta$ spectra and analysis. (A) Transient $\text{K}\beta$ emission signal of $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ in water. (B) Species associated spectra (SAS, red and blue) from a global analysis, invoking the model used for fitting the TA and $\text{K}\alpha$ kinetics and the reference difference spectra of Fig. 4D scaled by mapping the MLCT reference to SAS1.

leads to rapid excited state interconversion of the otherwise relatively long lived MLCT state. Furthermore, the ^3MC intermediate, which is expected to govern the MLCT decay, is stabilized to the point where it can be considered a well-isolated intermediate in the non-radiative relaxation. These changes in excited state dynamics reflect the solvent-dependent changes in the electronic structure of $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$. A qualitative molecular orbital (MO) diagram of $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ in weak Lewis acid solvent is shown in Fig. 7A. Both t_{2g} and e_g levels of the cyano-pyridyl complex increase upon substitution of bpy with CN^- ligands, as demonstrated by the reduction in the metal oxidation potential, the reduction in the MLCT excitation energy, and the elimination of the quintet state from the excited state relaxation pathway.^{1,2,39,44} These energetic changes in the redox potentials are readily explained by the σ and π^* energy levels of the CN^- ligand being of higher than the σ and π^* levels of bpy, as illustrated schematically in Fig. 7A. This MO picture is consistent with the projected potential energy surfaces (PES), calculated for $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ in DMSO, which are illustrated in a schematic form in Fig. 7B, based on the calculations in Zhang *et al.*¹

Increasing solvent Lewis acidity leads to a blue-shift of the MLCT absorption bands, as shown in Fig. 1. A similar solvation response has also been observed for Ru-centered cyano-pyridyls, where the solvent-dependent blue-shift has been shown to increase linearly with both the number of CN^- ligands and the Lewis acidity of the solvent.³⁹ The blue-shift is interpreted as a result of the high Lewis acidity solvent shifting electron density of

the CN^- orbitals away from the metal center, decreasing the $\pi(\text{CN}^-) \rightarrow d(\text{Fe})$ π -bonding and increasing the $d(\text{Fe}) \rightarrow \pi^*(\text{CN}^-)$ π -backbonding. Both of these changes stabilize the Fe t_{2g} levels relative to the (poly)pyridyl centered π^* levels (which are relatively unaffected by solvation).

The influence of lowering the t_{2g} levels on the PES is illustrated in Fig. 7C. The GS having 6 t_{2g} electrons is stabilized more than the MLCT and the ^3MC states each having 5 t_{2g} electrons, which are in turn stabilized more than the ^5MC state having only 4 t_{2g} electrons. Since the GS is stabilized the most, all excited states undergo an apparent destabilization since the PES in Fig. 7C are normalized relative to the ground state energy. Since the ^5MC state has two less t_{2g} electrons than the GS, and the ^3MC and MLCT states have one less t_{2g} electron than the GS, the relative destabilization of the ^5MC state is twice that of the ^3MC and MLCT states.

While the changes in the t_{2g} energy levels can be addressed by steady state measurements, the changes in e_g levels are most clearly addressed with transient measurements since the e_g levels only influence the metal centered electronic excited states. To explain the significant shortening of the MLCT lifetime of $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ in water relative to DMSO, the ^3MC state has to intersect the MLCT surface closer to its energy minimum. Therefore, the ^3MC state must be stabilized relative to the MLCT state, which indicates that the e_g levels also decrease in energy with increasing solvent Lewis acidity. This stabilization of the σ -bonded e_g orbitals is rationalized by the

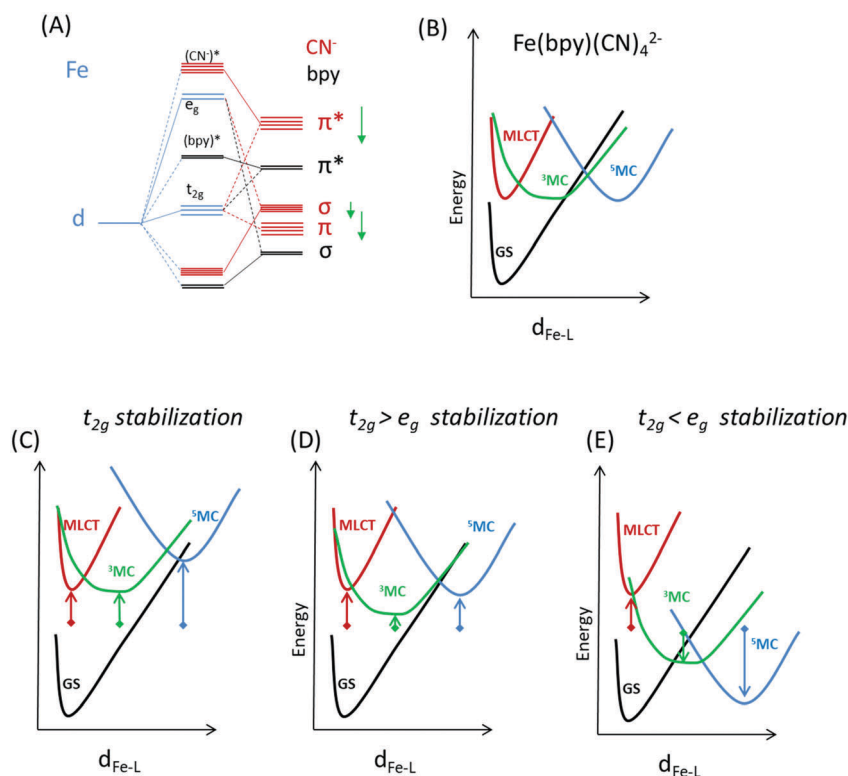


Fig. 7 (A) Schematic molecular orbital diagram for $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$. Green arrows indicate the shift in energy levels upon solvation in high Lewis acidity solvents. (B) Schematic of the potential energy surfaces of $[\text{Fe}(\text{bpy})(\text{CN})_4]^{2-}$ in low Lewis acidity solvents.¹ (C–E) Effect of variable t_{2g} and e_g orbital stabilization on the MLCT and MC excited state PES.

same argument for the π -bonded t_{2g} orbital stabilization discussed above. Stabilization of the e_g orbitals will shift down the 3MC and 5MC states relative to the illustration in Fig. 7C, which only accounts for the t_{2g} orbital stabilization. Two cases accounting for both t_{2g} and e_g stabilization are illustrated in Fig. 7D and E.

Stabilization of the e_g orbitals is consistent with the solvent dependence of the MLCT lifetimes in Ru-centered cyanopyridyls.⁴⁴ For these Ru complexes, the relationship between MLCT lifetime and solvent acceptor number (a measure of the solvent Lewis acidity) could be described by assuming that the 3MC energy was unchanged relative to the GS, requiring identical stabilization of the t_{2g} and the e_g levels. Interestingly, our experiments show that the 3MC lifetime, which is too short to be clearly observed in low Lewis acidity solvents,¹ is significantly extended in high Lewis acidity solvents, meaning that a reaction barrier for the inter-system crossing and internal conversion back to the GS is required. This reaction barrier can only arise by stabilizing the e_g levels by a smaller amount than the t_{2g} levels, such that the MC states are destabilized relative to the GS (Fig. 7D). If the e_g levels are destabilized equal to or more than the t_{2g} levels, then the MC states are stabilized with respect to the GS, as illustrated in Fig. 7E. In this case, it becomes impossible to arrange the potential energy surfaces such that there is a reaction barrier to the ground state, while maintaining a significant reaction barrier to the 5MC state consistent with the stabilization of the 3MC and 5MC states being proportionally with their number of e_g electrons. Since we observe no signature of the 5MC state in the excited state cascade, we conclude the ordering of the potential energy surfaces of $[Fe(bpy)(CN)_4]^{2-}$ in high Lewis acidity solvents match the illustration in Fig. 7D. In summary, the observation that the MLCT lifetime decreases with increasing solvent Lewis acidity shows that the e_g levels are stabilized in strong Lewis acid solvents, but not as strongly as the t_{2g} levels.

To support our interpretation of the solvent influence on the excited state energy levels, we have performed preliminary DFT calculations with a polarizable continuum description of both water and DMSO, and by including explicit water molecules at the N lone-pair site of the CN^- groups. The effects of implicit and explicit solvent interactions on the excited state energy levels are summarized in Table S1 in the ESI.[†] It is observed that there is virtually no difference between the energy levels calculated for water and DMSO when representing the solvents with continuum models. However, upon inclusion of the explicit waters at the N lone pair sites of the CN^- groups, the DFT calculations shows a destabilization of 3MLCT , 5MC , and 3MC states with respect to the ground state, in parallel to our experimental observations. In accordance with our interpretation of the experimental results, the calculations also show that the 3MLCT state is destabilized the most, and the 3MC state is destabilized the least. The minimum energy structures of our calculations (presented in Fig. S5, ESI[†]) shows that the water orients to form hydrogen bonds between to the cyanide N lone-pairs, supporting our interpretation of the experimental results that the reordering of the excited state level arises from explicit electronic interactions between solute and solvent.

Closing remarks

Combined ultrafast optical and XES measurements provide a clear picture for the MLCT excited state relaxation dynamics in $[Fe(bpy)(CN)_4]^{2-}$. In high Lewis acidity solvents, coordination of the CN^- ligands to the solvent significantly changes the lifetimes of the MLCT and the 3MC excited states relative to their lifetimes in low Lewis acidity solvents. The influence of the solvent on the excited state relaxation dynamics arise from inequivalent solvent stabilization of the CN^- and bpy energy levels, shifting the CN^- -influenced t_{2g} and e_g orbitals down relative to the bpy π^* levels, which in turn modifies the relative energies of the MLCT, 3MC , and 5MC excited state potential energy surfaces. Our study presents a clear identification and characterization of a metastable Fe-centered 3MC state in a hexacoordinated Fe centered complex.

Extracting this level of detail about the excited state relaxation mechanism has been made possible by the combined application of time resolved UV-visible TA and XES. Combining these techniques has allowed us to address not only the MLCT state dynamics, but also to identify the role of MC excited states in the electronic excited state relaxation, obtaining a more detailed picture of the excited state potential energy surfaces involved in the relaxation process. The increased robustness of the relaxation mechanisms extracted from the combined analysis of XES and TA measurements make them more amenable targets for computational quantum dynamics studies. Moreover, the relative simplicity of the Fe cyano-pyridyl compounds, and the fact that their potential energy landscape can be extensively modified by the choice of solvent, enabled a systematic exploration of the relationship between the potential energy landscape and the excited state lifetime and relaxation pathways.

These experiments also act as a stepping stone towards the investigation of Fe-centered photoactive molecular systems. With regards to future XES measurements, the good agreement with our reference spectra and the difference signal extracted from global analysis, provide further support for using the XES technique to identify the excited state species in 3d transition metal centered systems. With regards to future TA measurements, the clearly identified and isolated 3MC state presented here exhibit significant excited state absorption features throughout the visible spectrum. This should significantly help the assignment of excited state absorptions in future TA measurements on chemically related Fe coordination complexes.

Conflicts of interest

There are no conflicts to declare.

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Paper IV

Initial metal-metal breakage detected by fs X-ray scattering in $\text{Ru}_3(\text{CO})_{12}$ photolysis at 400 nm

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Initial metal-metal breakage detected by fs X-ray scattering in $\text{Ru}_3(\text{CO})_{12}$ photolysis at 400 nm

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ABSTRACT: Direct observation of selective chemical bond cleavage following photolysis, which is of great importance for controlled photocatalysis and photosynthesis, is challenging due to lack of proper experimental tools. Femtosecond X-ray pulses from X-ray free electron lasers are unique in providing the time resolution and structural sensitivity required for detection of chemical bond formation and breakage. The photolysis of the triangular cluster, $\text{Ru}_3(\text{CO})_{12}$, a prototype for the photochemistry of transition metal carbonyls and an important catalyst, provides a good example of the advantages of using femtosecond resolution X-ray solution scattering. We report the direct observation of photo-induced metal-metal bond cleavage in $\text{Ru}_3(\text{CO})_{12}$. The initial metal-metal bond cleavage leads to the formation of several transient structures, including an unknown one, in a cyclical reaction. We are able to track the structural kinetics: the Ru_3 ring opens due to metal-metal bond cleavage before 100 femtosecond, followed by CO loss and Ru_3 ring closure by re-establishment of the metal-metal bond after 10 picoseconds and the relaxation of intermediates to the starting molecule through CO recombination. The results indicate that contrary to long standing hypotheses, metal-metal bond breakage is the only chemical reaction immediately following photolysis of $\text{Ru}_3(\text{CO})_{12}$ and yield an experimentally verified mechanism of the complex photochemistry of $\text{Ru}_3(\text{CO})_{12}$.

Introduction

The intense femtosecond (fs) X-ray pulses of free electron lasers with time resolution of a few tens of fs offer unique opportunities to investigate the kinetics of the very early steps of photochemical reactions using pump-probe studies, as exemplified by tracking excited-state electronic structural dynamics,¹ direct observation of bond formation,² atomistic characterization of solvation dynamics,³ visualization of non-equilibrium dynamics,⁴ and in favorable cases observation of chemical bond dynamics of hot molecules.^{5,6} We have used fs X-ray solution scattering to study the photolysis of $\text{Ru}_3(\text{CO})_{12}$, a

thermally stable metal carbonyl which serves as prototype for the photochemistry of transition metal carbonyls and observed selective metal-metal (M-M) bond breakage.

$\text{Ru}_3(\text{CO})_{12}$ is not only an important catalyst, but also a synthetic precursor and building block in controlled photo-driven syntheses, whereby a specific chemical bond is broken at a specific wavelength.⁷⁻⁹ The UV-visible spectrum of $\text{Ru}_3(\text{CO})_{12}$ has two prominent absorption bands (Figure S1). The first at 390 nm originates from a metal bonding to antibonding ($4d\sigma \rightarrow 4d\sigma^*$) transition which has long been hypothesized to result in heterolytic cleavage of a M-M bond. The second band at 238 nm is attributed to

a metal to ligand charge transfer (MLCT) associated with the loss of a carbonyl ligand.¹⁰⁻¹²

Due to its theoretical and practical interest, the cleavage of a M-M bond in the photolysis of $\text{Ru}_3(\text{CO})_{12}$ has been extensively studied.¹³⁻¹⁷ The signals from ultrafast infrared (IR) spectroscopy following excitation of $\text{Ru}_3(\text{CO})_{12}$ in non-coordinating solvent like C_6H_{12} at 400 nm were interpreted as arising from two competing reactions, one involving metal-metal cleavage, the other with loss of a CO ligand. These reactions were concluded to both yield intermediates with bridging CO ligands: $\text{Ru}_3(\text{CO})_n(\mu\text{-CO})$ for the M-M cleavage channel and $\text{Ru}_3(\text{CO})_{10}(\mu\text{-CO})$ for the CO-loss channel.¹⁵ The CO-bridged intermediate $\text{Ru}_3(\text{CO})_n(\mu\text{-CO})$ was previously observed in an earlier time-resolved IR study.¹⁸ X-ray solution scattering with 100 ps resolution unambiguously confirmed the existence of $\text{Ru}_3(\text{CO})_{10}(\mu\text{-CO})$ but not $\text{Ru}_3(\text{CO})_n(\mu\text{-CO})$ and revealed an additional major intermediate $\text{Ru}_3(\text{CO})_{10}$ with terminal CO only following 400 nm excitation of $\text{Ru}_3(\text{CO})_{12}$ in C_6H_{12} .¹⁹ The existence of the major intermediate $\text{Ru}_3(\text{CO})_{10}$ was also confirmed by X-ray transient absorption spectroscopy with 100 ps resolution.²⁰

In the previous ultrafast IR¹⁵ and 100 ps resolution X-ray scattering studies^{9,19} mixtures of CO loss and M-M bond breakage intermediates were observed. These measurements lacked the structural sensitivity or time resolution to determine whether 400 nm excitation only leads to Ru-Ru bond dissociation with CO loss the product of a secondary process or if direct CO photodissociation can be achieved with 400 nm excitation. The origin of the major photoproduct at 100 ps, $\text{Ru}_3(\text{CO})_{10}$, also remained unclear. Successive single CO loss from $\text{Ru}_3(\text{CO})_{12}$ has been proposed,²¹ because simultaneous dicarbonyl loss from $\text{Ru}_3(\text{CO})_{12}$ in solution following single photon absorption at 400 nm is unlikely²¹ and has not been experimentally proven. In the present study we used the fs time resolution of the XPP end station²² at the LCLS X-ray Free Electron Laser²³ to determine the species formed immediately (~ 100 fs) after photoexcitation. The conditions of the previous experiments are summarized and compared with present ones in Table S1.

Methods

Experiments. The experiment was conducted over 36h in 12h shifts distributed over 3 consecutive days. New samples of $\text{Ru}_3(\text{CO})_{12}$ in C_6H_{12} with a concentration of 2 mM were prepared around every 6 hours in order to minimize possible sample degradation. In the pump-probe experimental setup the sample was continuously flowed through a 100 μm diameter capillary nozzle, after which it was collected and recycled. This procedure produces a free flowing circular liquid jet of 100 μm diameter with flow direction perpendicular to both the laser-pump and X-ray probe pulses. The flow speed of the jet was set to 1.5 ml/min yielding a flow velocity of 3 m/s ensuring that the sample is renewed between each laser-pump and X-ray probe event. The optical laser system at the XPP station of LCLS provided 14 μJ pump pulses at 400 nm with a full width at half maximum (fwhm) of 30 fs. These optical

pulses were focused to $\sim 100 \mu\text{m}^2$ on the liquid jet. To exclude multiphoton absorption and other nonlinear effects, the heating signals of the solvent were monitored as a function of laser power and 14 $\mu\text{J}/\text{pulse}$ was finally chosen to ensure good excitation ratio and single photon absorption. X-ray probe pulses were focused down to a spot size of $\sim 20 \mu\text{m}^2$ using beryllium lenses and set to spatially overlap with the laser pulses on the liquid jet.

The experiment was operated in beam-sharing mode with only the diamond (111) monochromatized part of the full LCLS beam going to the XPP instrument. The X-ray probe pulses (~ 40 fs fwhm) had $\sim 5 \times 10^{10}$ photons/pulse with an energy centered at 9.5 keV and $< 10^{-4}$ bandwidth and a frequency of 120 Hz. Due to the velocity mismatch between light and X-rays in C_6H_{12} , which displaces the temporal overlap of the pump and probe beams, the actual time resolution with a 100 μm liquid jet is ~ 100 fs.

Data reduction.

The X-ray scattering data was reduced following the methodology described in detail in previous work (SI of ref 3). The 2D X-ray patterns of laser-pumped/unpumped $\text{Ru}_3(\text{CO})_{12}$ in C_6H_{12} were recorded on the CSPAD detector developed at the LCLS.²⁴ For every seventh shot the scattering pattern of the solution was recorded without pump; from these scattering patterns the laser-off signals were constructed as described below. Each scattering pattern was corrected for solid angle, flat field and X-ray polarization. In addition, the output of the detector was corrected to reduce common mode fluctuations. A mask was then applied to the corrected 2D patterns to remove bad pixels and shadowed regions of the detector. Subsequently, the 2D images were azimuthally integrated into eleven slices, each spanning an angle of $\sim 32.5^\circ$, giving 11 $S(q)$ scattering curves for every X-ray shot as required to separate the isotropic and anisotropic components of the signal. The azimuthally integrated curves, $S(q)$, were corrected for the non-linear detector response.²⁵ The intensity corrected $S(q)$ were scaled to the theoretical scattering of a liquid unit cell of a 2 mM solution of $\text{Ru}_3(\text{CO})_{12}$ in C_6H_{12} in the q -region between 0.7-4.0 $\text{\AA}^{-1}$. This enables the determination of the excitation fraction of the solute and quantification of the energy release to the solvent. The average of the six nearest unpumped patterns was subtracted from each $S(q)$ curve with laser pump to create the difference signals, $\Delta S(q)$. Each $\Delta S(q)$ was time stamped with 10 fs fwhm resolution using the XPP timing tool²⁶ and sorted into time bins each containing ~ 2000 curves. The $\Delta S(q)$ in a given time bin were averaged after outlier rejection based on the in-set median of the $\Delta S(q)$. This resulted in 10-20% of the curves being discarded. This procedure was carried out for each of the eleven $S(q,t)$ producing eleven $\Delta S(q,t)$, which were used to separate the isotropic and anisotropic components of the signal.²⁷ Only the isotropic component of the signal was used for further analysis.

Quantum chemical (DFT) calculations.

To be consistent with previous X-ray solution scattering studies using 100 ps X-ray pulses,¹⁹ the geometries

of the starting molecule and of a non-exhaustive list of chemically plausible intermediates calculated previously (Figure S2) were used. The geometry of the new intermediate $\text{Ru}_3(\text{CO})_8(\mu\text{-CO})_3$, which was found indispensable to obtain a good fit at delays above 1.5 ps, was calculated using the same method.

MD simulations.

MD simulations on the solvent-solute interactions (cage structure) were performed using the same methods and program as previously (SI of ref 19) with OPLS all-atom force field on C_6H_{12} .²⁸ The all-atom Lennard-Jones potential parameters are listed below:

Solute		
Atom	σ (Å)	4ϵ (kJ/mol)
Ru	2.94	0.42
C	3.86	3.03
O	3.08	2.92

Solvent (C_6H_{12})		
Atom	σ (Å)	4ϵ (kJ/mol)
C	3.5	1.1
H	2.5	0.5

Briefly, one solute molecule ($\text{Ru}_3(\text{CO})_{12}$, $\text{Ru}_3(\text{CO})_{11}(\mu\text{-CO})$, $\text{Ru}_3(\text{CO})_{10}(\mu\text{-CO})$, $\text{Ru}_3(\text{CO})_8(\mu\text{-CO})_3$, $\text{Ru}_3(\text{CO})_{11}$ with all terminal CO, and CO molecule) was placed in a cubic box with a size of ~ 71.6 Å containing 2048 C_6H_{12} molecules. The simulations were performed at 300 K with a density of 0.781 kg/m^3 . Periodic boundary conditions were used and the Van der Waals interaction was cut off beyond 11 Å. The solute and solvent molecules were considered as rigid, no further geometry optimizations were applied during the simulations. The systems were equilibrated at 300 K over 200 ps at constant temperature, through coupling to a Nose-Hoover thermostat with a time constant of 0.3 - 0.7 ps, depending on the system. The step size was 0.5 fs; the simulations were performed in the NVT ensemble and the trajectories were followed for up to 1.8 ns.

Results and Discussion

The kinetics is modeled by analyzing the experimental difference scattering patterns at different times using linear combinations of the difference scattering patterns of putative intermediates from DFT calculations. This approach relies on the assumption that the time and spatially averaged structures of the intermediates, the only ones accessible by X-ray scattering, do not differ too much from those of the equilibrium structures of putative intermediates.

The total scattering signal arises from three contributions, scattering from the solute, solvent and solute-solvent interaction (cage) as described earlier^{9,19} and in

Figures S3-S5. These model difference X-ray scattering intensities (Figures S3b and S3c) confirm that each species generates a distinct difference scattering signal that makes ultrafast X-ray scattering a tool to detect all transient structures including optically silent species.^{9,19} In our previous studies we considered an extensive set of potential reaction intermediates (Figure S2). Only $\text{Ru}_3(\text{CO})_{10}(\mu\text{-CO})$ and $\text{Ru}_3(\text{CO})_{10}$ were found indispensable to fit the experimental data at times above 50 ps. In order to obtain a good fit at time delays below 10 ps in the present study, it was necessary to include $\text{Ru}_3(\text{CO})_{11}(\mu\text{-CO})$, which had so far only been characterized by its IR signature,^{15,18} and a new intermediate, the triple-bridge $\text{Ru}_3(\text{CO})_8(\mu\text{-CO})_3$ (Figure S3a) exhibiting a broken M-M bond. The other intermediate with similar structure $\text{Ru}_3(\text{CO})_9(\mu\text{-CO})_3$ (isomer2 in Figure S2) did not give a good fit. $\text{Ru}_3(\text{CO})_{11}$ with terminal CO only was initially assumed to be the precursor of $\text{Ru}_3(\text{CO})_{10}(\mu\text{-CO})$ ^{7,15} and included in the fit, but rejected as it did not improve matters as illustrated in Figures 1b and 1c. Figure 1a displays a set of difference signals, $q\Delta S(q,t)$, where $q = 4\pi\sin(\theta)/\lambda$, 2θ is the scattering angle and λ the X-ray wavelength 1.305 Å, representing key features at fs and ps time delays. As illustrated in Figure S5, the strong negative feature at $q = 1.3 \text{ Å}^{-1}$ and signals below this value arise mainly from solvent heating,²⁹ the positive shoulder at $1.4 < q < 1.8 \text{ Å}^{-1}$ is a combination of solute and cage with slight contribution from solvent, while signals at $q > 2 \text{ Å}^{-1}$ arise mainly from changes in solute structure. These signals display distinct features revealing that different transient structures are formed. The significant positive feature at $q = 4 \text{ Å}^{-1}$ at $t = 100$ fs is split at 5.16 ps, following which the difference signal evolves to a broad oscillation from $q = 2.3 \text{ Å}^{-1}$ to $q = 4.5 \text{ Å}^{-1}$ at 45 ps. Comparison of the experimental $q\Delta S(q,t)$ with those arising from different transient structures illustrate that $\text{Ru}_3(\text{CO})_{11}(\mu\text{-CO})$ (M-M broken, single bridge) is the only species at the onset of the reaction (Figure 1b), while the $q\Delta S(q,t)$ arising from $\text{Ru}_3(\text{CO})_8(\mu\text{-CO})_3$ best describes the data at $t = 5.16$ ps (Figure 1c). When all intermediates were included in the fit, only $\text{Ru}_3(\text{CO})_{11}(\mu\text{-CO})$ and $\text{Ru}_3(\text{CO})_8(\mu\text{-CO})_3$ remained at 100 fs and 5.16 ps respectively, while the contribution of other intermediates converged to zero. The $q\Delta S(q,t)$ at $t = 45$ ps is fully consistent with our previous X-ray scattering data at 50 ps collected with synchrotron radiation (Figure 1d), where $\text{Ru}_3(\text{CO})_{10}$ was determined to be the major photoproduct.¹⁹

To elucidate the reaction kinetics a two-step approach of single-point and global analysis was applied (detailed in the Supporting Information, SI). The experimental $q\Delta S(q,t)$ at 170 different time delays were fitted (Figure S6) to obtain the kinetics. The single-point procedure yields the concentration of each species at each time delay as shown by the individual markers in Figure 2. Even though the results of this analysis have significant uncertainties, as evident from the scatter in Figure 2, they allow the identification of a potential kinetic model that can be applied within a global fitting analysis. In this second step of the analysis the time evolution of each transient

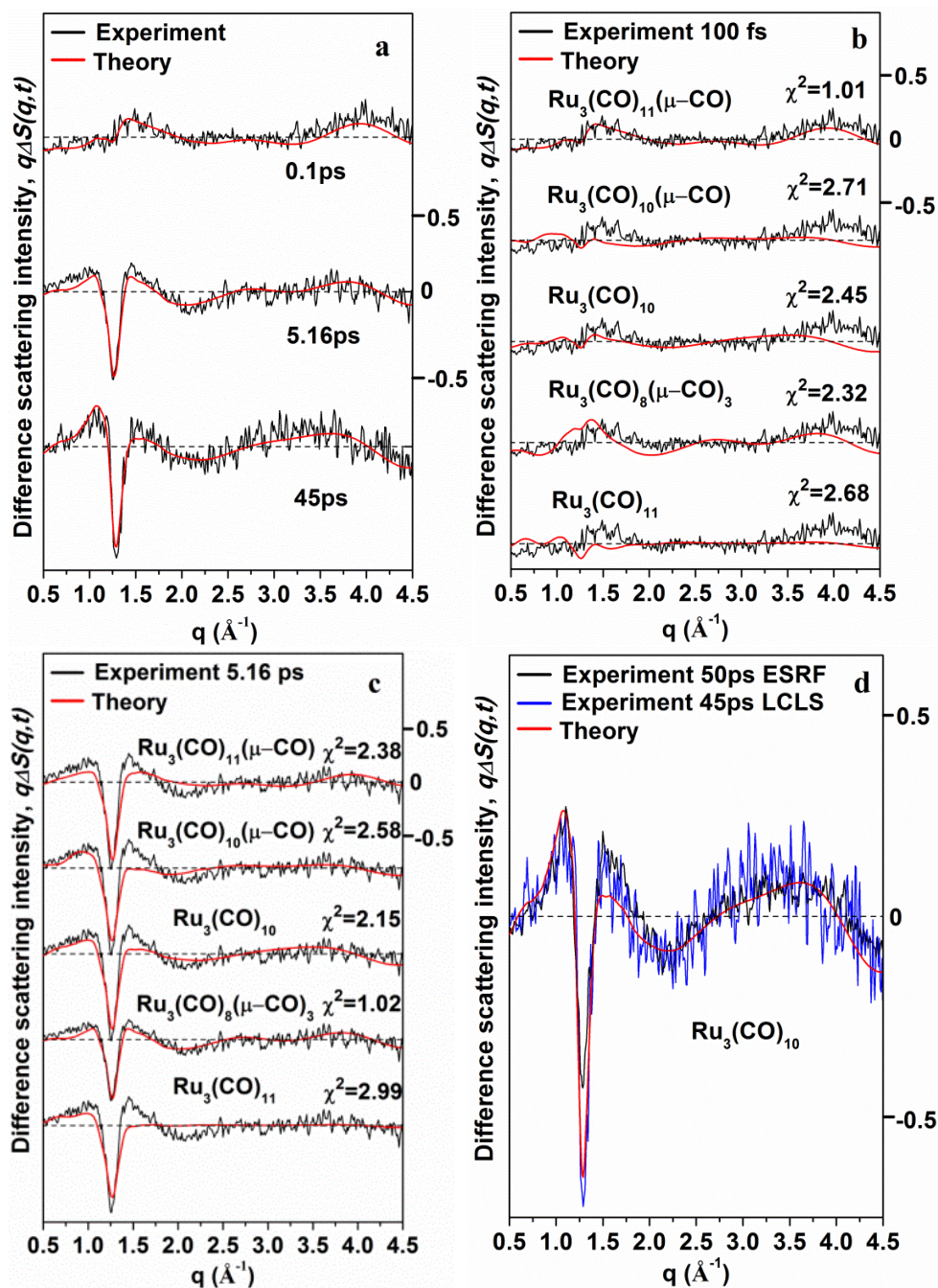


Figure 1. Difference X-ray scattering intensities, $q\Delta S(q,t)$. a, $q\Delta S(q,t)$ at 100 fs, 5.16 ps and 45 ps. Distinct features are evidence that different transient structures dominate at different time delays. b, $q\Delta S(q,t)$ at 100 fs (black) compared with the simulated difference signal (red) of individual candidate molecular structures used in the linear combination fit. Best agreement between experiment and theory at 100 fs is obtained with $\text{Ru}_3(\text{CO})_{11}(\mu\text{-CO})$. c, For $q\Delta S(q,t)$ at 5.16 ps (black) compared with the simulated difference signal (red) the best agreement is obtained with $\text{Ru}_3(\text{CO})_8(\mu\text{-CO})_3$. When all intermediates were included in the fit, only $\text{Ru}_3(\text{CO})_{11}(\mu\text{-CO})$ and $\text{Ru}_3(\text{CO})_8(\mu\text{-CO})_3$ remained at 100 fs and 5.16 ps respectively, while the contribution of other intermediates converged to zero. d, The experimental data at 45 ps are consistent with 50 ps data of previous time-resolved synchrotron X-ray scattering studies where $\text{Ru}_3(\text{CO})_{10}$ was determined to be the major photoproduct.¹⁹ The difference between the two data sets at $q = 1.3 \text{ \AA}^{-1}$ comes from the solvent signals due to different laser power. Broken lines indicate the zero level of each curve in a, b, c and d.

species is constrained to conform to a kinetic model allowing robust determination of the reaction constants. The global fitting is described in detail in SI and in Figure S7. The full lines in Figure 2 illustrate the time evolution of each species following this more quantitative analysis.

At the onset of the reaction only the M-M breakage transient structure $\text{Ru}_3(\text{CO})_{11}(\mu\text{-CO})$ is formed. It loses one CO ligand to form $\text{Ru}_3(\text{CO})_8(\mu\text{-CO})_3$ at 1.5 ps with a reaction rate constant of $6.6 \pm 0.5 \times 10^{11} \text{ s}^{-1}$. This triple-bridge $\text{Ru}_3(\text{CO})_8(\mu\text{-CO})_3$ has three absorption bands originating from the stretching mode of bridging CO which either overlap with the absorption of $\text{Ru}_3(\text{CO})_{11}(\mu\text{-CO})$ or the terminal CO, as illustrated in Figure S8. It may therefore have escaped detection in time-resolved IR studies.¹⁵ Together with our previous 100 ps X-ray scattering studies,^{9,19} this is another example illustrating the advantage of ultrafast X-ray scattering in the detection of optically silent transient structures.

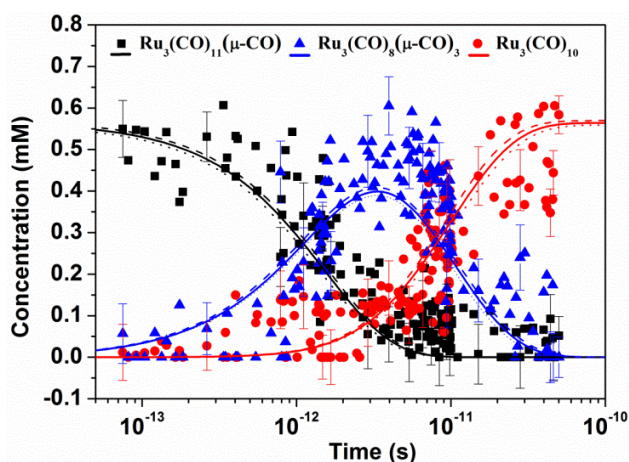


Figure 2. Evolution of the population of transient species as a function of time: $\text{Ru}_3(\text{CO})_{11}(\mu\text{-CO})$ (black), $\text{Ru}_3(\text{CO})_8(\mu\text{-CO})_3$ (blue) and $\text{Ru}_3(\text{CO})_{10}$ (red). Scatter plots are the result of the analysis of individual time delays while the solid curves correspond to global fitting. The dashed and dotted lines represent the time course of the concentrations for reaction rate constants on two sides of the 95% confidence level. Error bars obtained from the standard deviations of the experimental data are shown for one out of ten time points only for clarity. The maximum concentration of $\text{Ru}_3(\text{CO})_{11}(\mu\text{-CO})$ (0.56 mM) corresponds to 28% conversion in the photolysis.

$\text{Ru}_3(\text{CO})_8(\mu\text{-CO})_3$ transforms into $\text{Ru}_3(\text{CO})_{10}$ at 10 ps with a reaction rate constant of $1 \pm 0.2 \times 10^{11} \text{ s}^{-1}$ by loss of a further CO. $\text{Ru}_3(\text{CO})_{10}$ becomes the major transient structure after 10 ps. A reduced kinetic model without the triple-bridge intermediate was evaluated against the full model involving the $\text{Ru}_3(\text{CO})_8(\mu\text{-CO})_3$ using a statistical F-test. We conclude with 99.7% confidence that the full kinetic model represents the experimental data better. The F-test evaluation is described in SI, and the result is shown in Figure S9. A direct comparison of the experimental difference X-ray scattering intensity $q\Delta S(q,t)$ at 5.16 ps with the reduced and the full model also confirms the formation of $\text{Ru}_3(\text{CO})_8(\mu\text{-CO})_3$ (Figure S10 in SI).

Femtosecond X-ray solution scattering clearly demonstrates the selective M-M breakage of $\text{Ru}_3(\text{CO})_{12}$ when excited at 400 nm and excludes any competing primary reactions. The origin of the major photoproduct $\text{Ru}_3(\text{CO})_{10}$ previously observed in 100 ps X-ray studies^{9,19,20} is also simply explained by the full model. It is formed through successive CO loss from $\text{Ru}_3(\text{CO})_{12}$ via two intermediates $\text{Ru}_3(\text{CO})_{11}(\mu\text{-CO})$ and $\text{Ru}_3(\text{CO})_8(\mu\text{-CO})_3$. The time course of the weights of the two solvent components is also obtained from the data fitting and shown in Figure S11. A detailed description of the solvent contribution can be found in the SI.

To obtain direct information about the molecular structure of the reaction intermediates and infer the reaction mechanism, the solute-only difference signal was obtained by subtracting the contribution from bulk solvent response and changes in the solvation cage structure (by MD simulations) from the measured signals.⁹ In Figure 3a the solute-only difference signals at three key time delays are compared with the difference signal of the intermediates determined to be dominating at those time delays and in each case good agreement between the model and the data is observed.

Whereas in spectroscopy the signatures of particular intermediates correspond to specific energies, in solution scattering the structural information is spread over the entire q -range. A more intuitive picture of the structural rearrangements is therefore provided by the difference Radial Distribution Function (DRDF) $r\Delta R(r,t)$ i.e. the sine transform of $q\Delta S(q,t)$ (described in SI), which represents the atom-atom pair distribution function during the course of the reaction. A positive peak in the DRDF indicates the presence of a new characteristic correlation length in the molecule, while a negative peak indicates loss of such a correlation length, often representative of a broken chemical bond. The experimental and theoretical $r\Delta R(r,t)$ at 100 fs, 5.16 ps and 45 ps shown in Figure 3b provide structural information about $\text{Ru}_3(\text{CO})_{11}(\mu\text{-CO})$, $\text{Ru}_3(\text{CO})_8(\mu\text{-CO})_3$ and $\text{Ru}_3(\text{CO})_{10}$, which are the dominant solute species at these time delays. Strong positive peaks at 5.2 Å at 100 fs and 5.4 Å at 5.16 ps are observed, which disappear at 45 ps. These arise from the newly formed long Ru...Ru distances in $\text{Ru}_3(\text{CO})_{11}(\mu\text{-CO})$ and $\text{Ru}_3(\text{CO})_8(\mu\text{-CO})_3$. The negative peaks at 2.9 Å at 100 fs, 3.5 Å at 5.16 ps and 3.3 Å at 45 ps correspond to the broken Ru-Ru bond compared to the parent molecule.

Some caution is, however, necessary when interpreting DRDFs, as both a limited q -range and peak overlap may lead to shifts in peak positions (Figure S12 in SI). The different negative peaks in Figure 3b arise from differently overlapped Ru-Ru distances in $\text{Ru}_3(\text{CO})_{11}(\mu\text{-CO})$, $\text{Ru}_3(\text{CO})_8(\mu\text{-CO})_3$ and $\text{Ru}_3(\text{CO})_{10}$ with that in the parent molecule. The positive peaks of the long Ru...Ru distance in $\text{Ru}_3(\text{CO})_{11}(\mu\text{-CO})$ and $\text{Ru}_3(\text{CO})_8(\mu\text{-CO})_3$ are also shifted by about 0.2 Å compared to the molecular structures used to simulate the curves. With this offset in mind, the structural changes of the Ru_3 cluster following photolysis can be clearly visualized from the

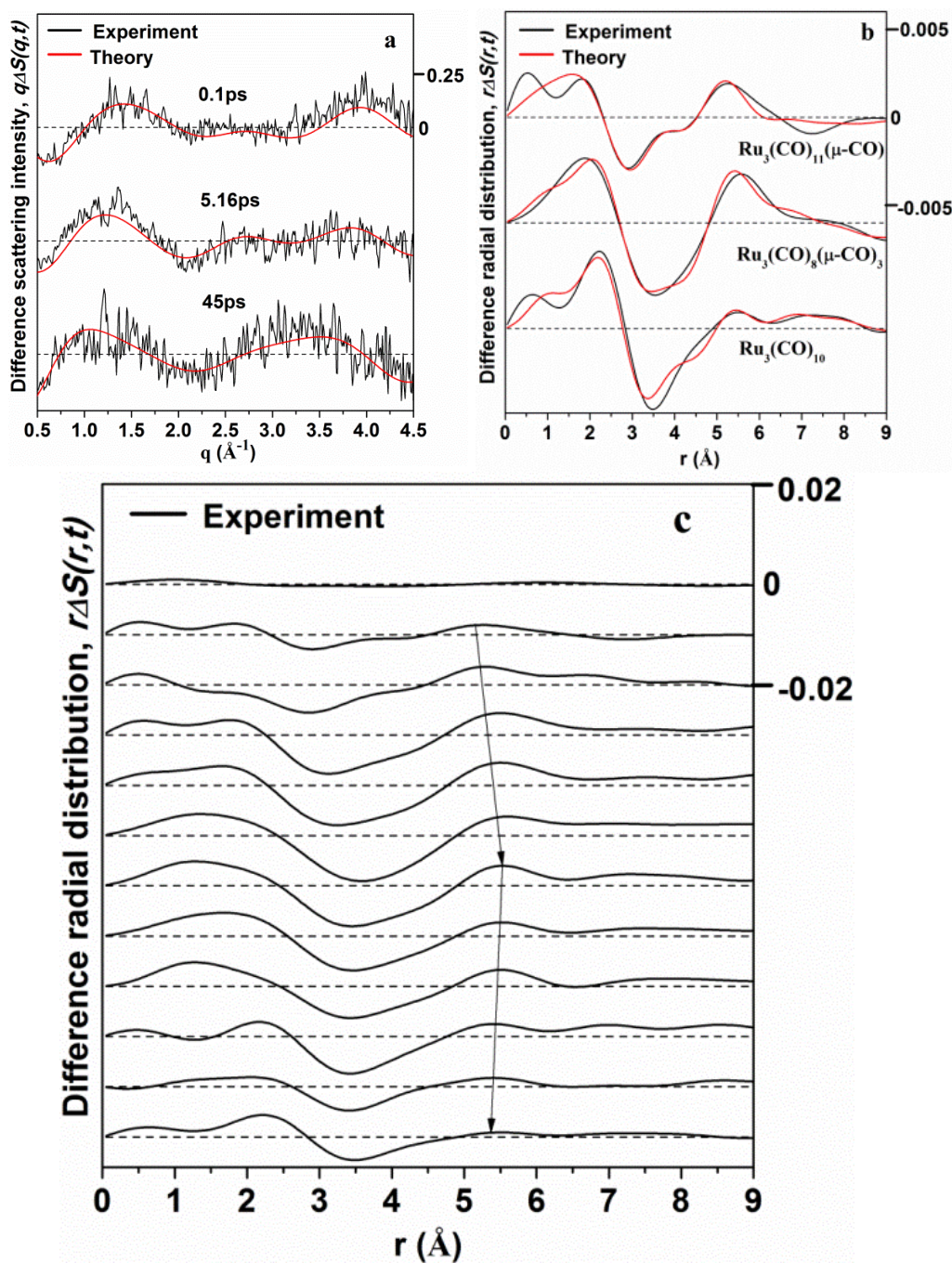


Figure 3. Solute-only difference scattering intensities and radial distribution functions. **a**, Solute-only experimental (black) and theoretical (red) difference scattering intensities $q\Delta S(q,t)$ at 100 fs, 5.16 ps and 45 ps. **b**, Solute-only difference radial distribution functions $r\Delta S(r,t)$, obtained by Fourier sine transform of **a**. **c**, Selected experimental solute-only difference radial distribution functions $r\Delta S(r,t)$ at different time delays: from top to bottom -1 ps, 100 fs, 95 fs, 760 fs, 1.23 ps, 3.79 ps, 5.16 ps, 6.51 ps, 6.94 ps, 9.87 ps, 41 ps, 45 ps. Broken lines indicate the zero level of each curve in **a**, **b** and **c**.

DRDFs presented in Figure 3c, illustrating the appearance of the positive peak at 5.2 $\text{\AA}$ at the onset of the reaction, its gradual shift towards longer distances in the middle of the reaction and its final disappearance at the end. In our previous synchrotron study with higher q -space coverage, the DFT calculated structures of $\text{Ru}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{10}$

were optimized by direct structural fitting and a scaling factor for the DFT prediction was determined (Table S2). Applying the same scaling factor to the DFT optimized structure of $\text{Ru}_3(\text{CO})_8(\mu\text{-CO})_3$ yields Ru-Ru distances of 2.73, 2.83, and 5.18 $\text{\AA}$.

Combining the information from time-resolved IR results,¹⁵ with the results of our previous study from 50 ps to 300 ns,^{9,19} and the current study from 100 fs to 50 ps, we propose in Figure 4 a revised and more complete mechanism for the photofragmentation of Ru₃(CO)₁₂ in C₆H₁₂ following 400 nm excitation. 400 nm laser excitation selectively breaks a single Ru-Ru bond to form Ru₃(CO)₁₁(μ-CO). No competitive CO loss reaction is detected. Ru₃(CO)₁₁(μ-CO) loses one CO forming Ru₃(CO)₈(μ-CO)₃ with a characteristic timescale of 1.5 ps, which in turn loses another CO and also reforms the M-M bond to yield Ru₃(CO)₁₀ on a time scale of 10 ps. Ru₃(CO)₁₀ dominates from 10 ps to 100 ns,^{9,19} and rebinds one CO to form Ru₃(CO)₁₀(μ-CO),^{9,15,19} which eventually relaxes to the starting molecule by binding another CO.

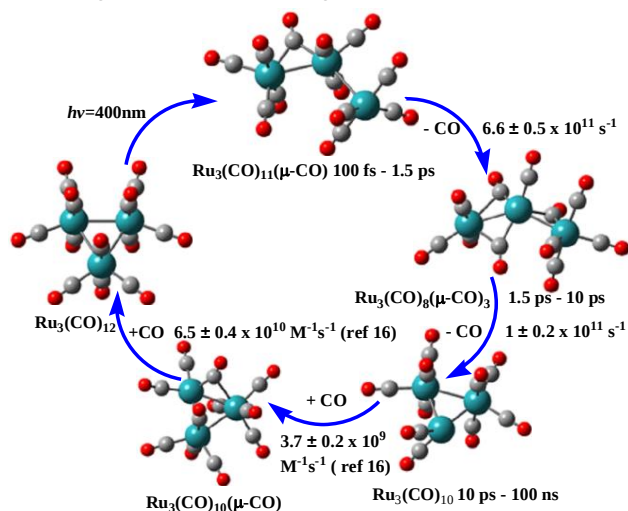


Figure 4. Reaction pathway of photocleavage of Ru₃(CO)₁₂ in C₆H₁₂ following 400 nm excitation. Laser excitation breaks one Ru-Ru bond to form Ru₃(CO)₁₁(μ-CO), which loses one CO to form Ru₃(CO)₈(μ-CO)₃ at 1.5 ps. The latter loses another CO and yields Ru₃(CO)₁₀ at 10 ps. Ru₃(CO)₁₀ dominates from 10 ps to 100 ns, and rebinds one CO to form Ru₃(CO)₁₀(μ-CO) which eventually relaxes to the starting molecule by binding another CO. Ru: cyan, C: gray, O: red.

Conclusion

We demonstrated that fs X-ray solution scattering is a robust tool to observe the transient structural kinetics of chemical bond cleavage at the very early stage of a photochemical reaction (Figure 3c), and reveal optically silent intermediates. We expect that our findings of the selective metal-metal bond cleavage at 400 nm and the formation of two intermediates with single Ru-Ru bond cleavage: Ru₃(CO)₁₁(μ-CO) and Ru₃(CO)₈(μ-CO)₃, with lifetimes of a few picoseconds will influence the protocols in controlled photocatalysis and photosynthesis.

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Paper V

An ultrafast molecular movie reveals that dispersion interactions control the photochemistry of diiodomethane in solution.

Matthijs R. Panman, Elisa Biasin, Oskar Berntsson, Markus Hermann, Stephan Niebling, Ashley J. Hughes, Joachim Kübel, Kalina Atkovska, Emil Gustavsson, Asmus O. Dohn, **Mads G. Laursen**, Diana B. Zederkof, Alireza Honarfar, Kensuke Tono, Tetsuo Katayama, Sigeki Owada, Tim Brandt van Driel, Kasper Kjær, Martin M. Nielsen, Jan Davidsson, Jens Uhlig, Kristoffer Haldrup, Jochen S. Hub, Sebastian Westenhoff.

An ultrafast molecular movie reveals that dispersion interactions control the photochemistry of diiodomethane in solution.

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One sentence summary: Filming a chemical reaction yields a new reaction scheme and surprising properties of an intermediate encounter complex.

Molecules must encounter one another before they can react. The properties of the resulting encounter complexes strongly influence the rate and outcome of reactions. Despite the frequent occurrence of encounter complexes, their observation remains elusive. Here, we measure the structural dynamics of photodissociation and recombination of diiodomethane in cyclohexane with femtosecond time-resolved wide-angle X-ray scattering. Contrary to established expectations, we find that the transient radical pairs remain confined to a common solvent cavity for over 500 ps. Quantum chemical calculations indicate that dispersion forces stabilize the encounter complex. We also find that 40 % of the pairs do not recombine, which we assign to spin-forbidden recombination. Characterizing the radical encounter pair allows us to revise the reaction mechanism and suggests that even relatively weak dispersion forces can critically influence the outcome of chemical reactions.

The properties of encounter complexes (or pairs) critically determine the rates and products of chemical reactions (1). This is reflected in the Arrhenius equation $A \cdot \exp(-E_A/RT)$, which describes the rate of chemical reactions. The exponential term relates to the transition state of the reaction (2) which is described in terms of the activation energy E_A and temperature T (R is the gas constant). The ‘prefactor’ A describes the attempt frequency of crossing the energy barrier (3) and depends strongly on the properties of the encounter complex, such as lifetime, spatial arrangement, and solvent interaction (4). Encounter complexes are important in enzymatic and artificial catalysis.

Despite their importance and the large amount of scientific work that has been dedicated to it (1), it is still challenging to directly detect and characterize encounter complexes. Since covalent bonds are not yet formed, encounter pairs are spectrally dark, which severely limits the use of time-resolved spectroscopic techniques as investigative tools (2, 5, 6). Electron and nuclear magnetic resonance spectroscopy are in principle sensitive to the structure of encounter pairs, but lack time-resolution to detect the typically short-lived complex.

Here, we investigate the formation and annihilation of encounter pairs in the photodissociation of diiodomethane (CH_2I_2). Absorption of 266 nm light leads to impulsive C–I bond scission, yielding a transient radical pair $\text{CH}_2\text{I}^\bullet + \text{I}^\bullet$ (7) (see Fig. 1A). The radicals are the encounter complex for the recombination reaction, which yields an isomer $\text{CH}_2\text{I}-\text{I}$ (8, 9). The mechanism of isomer formation is not understood and has been suggested to proceed directly (within 100 fs to 1 ps) (10, 11) or through recombination of radicals, which reside in the same solvent cage (1 ps to 20 ps) (8). Approximately 70 % of the radicals form isomers on picosecond time scales (8). The main loss pathway is believed to be solvent-cage escape of the radicals. The recombination of these separated radicals has been ascribed to isomer formation on nanosecond timescales (8). The reaction mechanism has been derived from time-resolved spectroscopy experiments, which, inherently, are not sensitive to the structure and lifetime of the radical encounter pairs.

To resolve the structural changes in solution (12), we investigated the reaction using time-resolved wide-angle X-ray scattering (WAXS) at an X-ray free electron laser (13–17). The measurements were conducted at the X-ray pump-probe (XPP) instrument at the Linac Coherent Light Source (LCLS) XFEL facility (data in main text) (18) and experimental hutch (EH) 2 of beam line (BL) 3 at Spring-8 Angstrom Compact free electron LASER (SACLA) (data in the Supplementary Information) (19). At the LCLS, the sample was supplied in the form of a round liquid jet with a diameter of 50 μm . The reaction was triggered using laser pulses at 266 nm

(<70 fs Full-Width Half-Maximum, FWHM) and probed at different time delays t after the excitation event by recording the scattering of short X-ray pulses at 9.5 keV (<50 fs FWHM). For delay times $t < 2$ ps we used the timing diagnostic at the beam line (20). The overall time-resolution was 90 fs limited by the durations of the X-ray (50 fs) and UV (70 fs) pulses and their velocity mismatch in the liquid (50 fs).

The procedure for the correction and reduction of the data is detailed in the materials and methods (21). Briefly, difference scattering patterns were constructed by subtracting scattering patterns collected with and without optical excitation. The difference scattering patterns were sorted according to their time stamp and averaged. Subsequently, the averaged difference scattering patterns were azimuthally integrated in 15 slices, from which the isotropic and anisotropic difference scattering signals, $\Delta S(q, t)$ as a function of scattering vector q and delay time t , were extracted (22). The azimuthally averaged signals can be interpreted as the scattering signals arising from randomly distributed molecules in solution (see Fig. S3). We measured the heat response of the solvent in a separate experiment using a dye molecule (see figure S4A) and removed it from the CH₂I₂ dataset (details in materials and methods (21); see Fig. S5 and Fig. S6). We further included the solvent-heat response in the structural fit (see below) to compensate for an imperfect subtraction.

The heat-subtracted difference-scattering curves are shown in Fig. 1B. The creation or destruction of inter-atomic distances directly results in changes in the amplitude of the scattering signal at different scattering vectors. For the first 400 fs we observe oscillatory signals along the q -axis, which increase in intensity and shift in q position. For $t > 400$ fs, we observe variations at different regions in q which indicates evolving chemical species. An inverse sine-Fourier transformation of $\Delta S(q, t)$ yields the real-space representation of the data ($r^2\Delta S(r)$, Fig. 1C), which now directly reveal the evolving inter-atomic distances. The positions of the negative peaks at ~ 3.54 Å and ~ 2.2 Å represent ground state distances. These distances are depleted re-

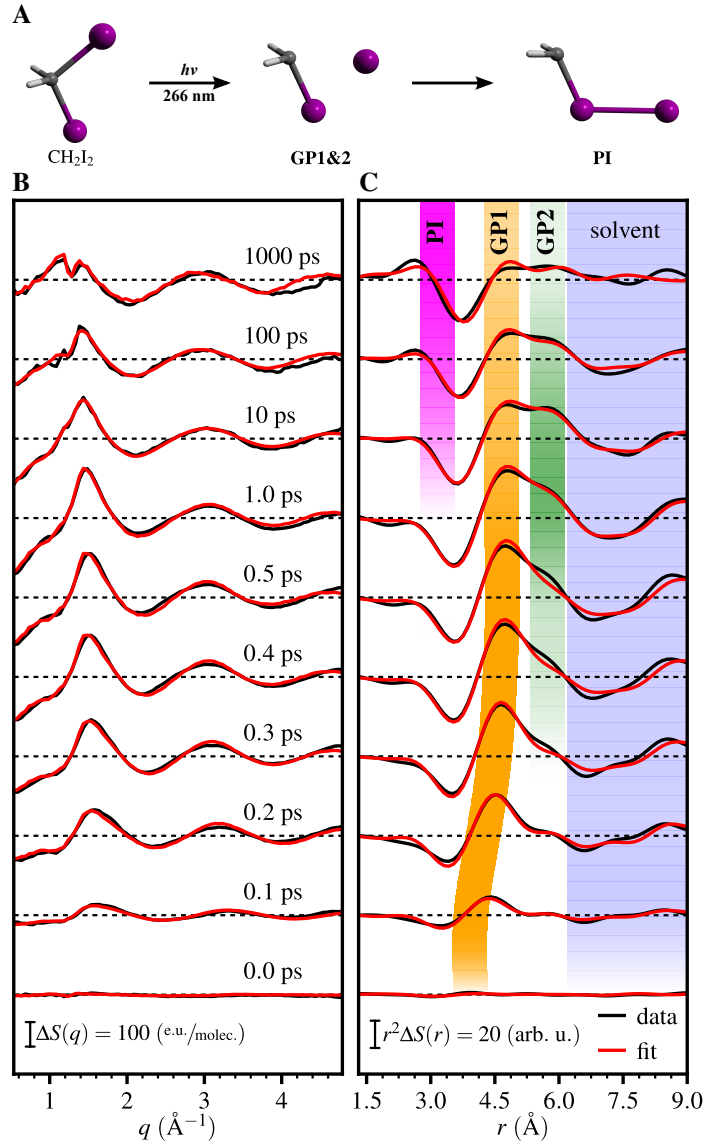


Figure 1: **The real-time photo-dissociation of CH_2I_2 and the resulting photochemical species are visualized directly with femtosecond time-resolved WAXS.** Panel A: Schematic ball-and-stick representation of the photodissociation of diiodomethane CH_2I_2 and subsequent formation of the transient isomer $\text{CH}_2\text{I}-\text{I}$ (**PI**). Panel B: Structural least-squares fit (red) of the difference scattering (black, $\Delta S(q)$) for a range of time delays after laser excitation (labeled in the plot) in reciprocal space (q). Panel C: Real-space representation (r) of the difference scattering ($r^2\Delta S(r)$) and structural fits obtained by a sine-Fourier transformation of the data shown in panel A. The colored bands are centered on the $\text{I}\cdots\text{I}$ separation distance of the **PI**, **GP1**, and **GP2** species obtained from the fit. The color coding corresponds to that used in Fig. 2A. The solvent term (cage ΔS_{IS} and displaced volume ΔS_{SS} , collectively shown in blue) predominantly contributes to the difference scattering at distances $r \geq 6.2 \text{ \AA}$.

spectively due to the loss of the $I \cdots I$ distance and $C-I$ bond in CH_2I_2 . The positive peaks arise from characteristic atom-atom distances in the newly formed photo products. A single positive peak is visible at delay times $t < 300$ fs (geminate pair 1, **GP1**, orange band in Fig.1C). We assign this peak to the $I \cdots I$ distance between the $I^\bullet$ and $CH_2I^\bullet$ fragments. The r -position of this peak increases continuously for times $t < 400$ fs, after which it remains constant at $r = 4.65$ Å.

For $t > 300$ fs, a satellite peak appears (**GP2**, green band in Fig.1B). Geometric considerations indicate that the **GP1** and **GP2** peaks at 4.65 Å and 5.75 Å correspond to the $I \cdots I$ separations when the $I^\bullet$ fragment is situated at, respectively, the I and CH_2 hemispheres of the $CH_2I^\bullet$ fragment (see Fig. 2C). This assignment is directly supported by molecular dynamics (MD) simulations (see Fig. S11). Thus, the two peaks (**GP1** and **GP2**) represent two possible relative arrangements of the fragments within the mutual solvent pocket. Initially, only **GP1** is formed. However, rotational diffusion of the $CH_2I^\bullet$ and $I^\bullet$ fragments leads to an equilibration between the two possible arrangements. For $t > 1$ ps, the amplitudes of the **GP1** and **GP2** peaks decrease at the same rate (see Fig. 2A for more time points). In the same time range, a positive peak appears at 3.2 Å which indicates the formation of the $I-I$ bond in the photoisomer (**PI**, magenta band in Fig.1B) (9). The blue band at $r \geq 6.2$ Å denotes the distances which are affected by changes in the solvent-shell structure of the reacting molecules.

To quantify these observations and to extract the $I \cdots I$ distances and relative concentrations of the reaction products, we performed a least-squares fit of model-scattering curves to the data in q -space (structural modeling, red curves in Fig. 1B). The solute term of the scattering was calculated using the Debye equation (see Eq. S6). Solute-solvent contributions were obtained through the forward sine-Fourier transform of the pair distance distribution function (PDF) between the iodine and the solvent atoms derived from MD simulations (see Eq. S7). We constructed a library of 124 PDFs for 2 iodine atoms constrained at distances spanning from 0 Å to 15 Å. Finally, the change in the shape of the solvent cavity occupied by the solute was

calculated with the Debye equation using atoms with form factors derived from the PDF (see Eq. S10 and Fig. S9 in the materials and methods (21) for details).

The data were fit by optimizing the I $\cdots$ I distances and amplitudes of the ground state and three reaction products, corresponding to geminate pairs **GP1**, **GP2**, and the photoisomer **PI**. The quality of the fit is excellent in both reciprocal- and real-space (Fig. 1B and C). Minor deviations occur at $r \approx 2.8$ Å, which is due to the loss of the C–I bond in CH₂I₂ and which was not considered in the modeling, and at $r \geq 6.2$ Å in the solvent region. The equilibrium I $\cdots$ I distance of **PI** was 3.16 ± 0.02 Å which is in good agreement with literature (9). The equilibrium I $\cdots$ I distances of **GP1**, and **GP2** were refined to 4.66 ± 0.01 Å and 5.75 ± 0.01 Å, respectively.

In order to capture the initial dynamic evolution of the bond length, the I $\cdots$ I distance of **GP1** (Fig. 1B) was allowed to change with time for $t < 500$ fs. We found that it increases linearly with time (Fig. 2B), mimicking a free-flying object in space. The relative velocity between the radicals during the free-flight phase was 2.8 ± 0.1 Å ps^{−1}. After 250 fs, the velocity of the fragments decreases rapidly until the equilibrium position of 4.65 ± 0.01 Å is reached at ~ 300 fs. We attribute the deceleration of the I $\bullet$ radicals to their collision with solvent molecules. The gradual deceleration of the fragments (as opposed to an abrupt stop) indicates a distribution of flight paths or velocities across the ensemble. We do not observe an acceleration phase. This may be due to the large uncertainty on the first data points in the “free flight” phase or insufficient time-resolution of the experiment (90 fs). We also note that the **GP1** peak in Fig. 2B does not broaden after 250 fs, which indicates that the overwhelming majority of fragments are stopped by collision with the solvent cage.

Inspection of the time-dependent amplitudes of the structural fit (Fig. 2A) confirms the qualitative observations drawn above. We observe a sub-picosecond rise of **GP2** which coincides with the decay of **GP1** confirming that **GP2** is formed from **GP1**. For $t > 1$ ps, **GP1** and **GP2**

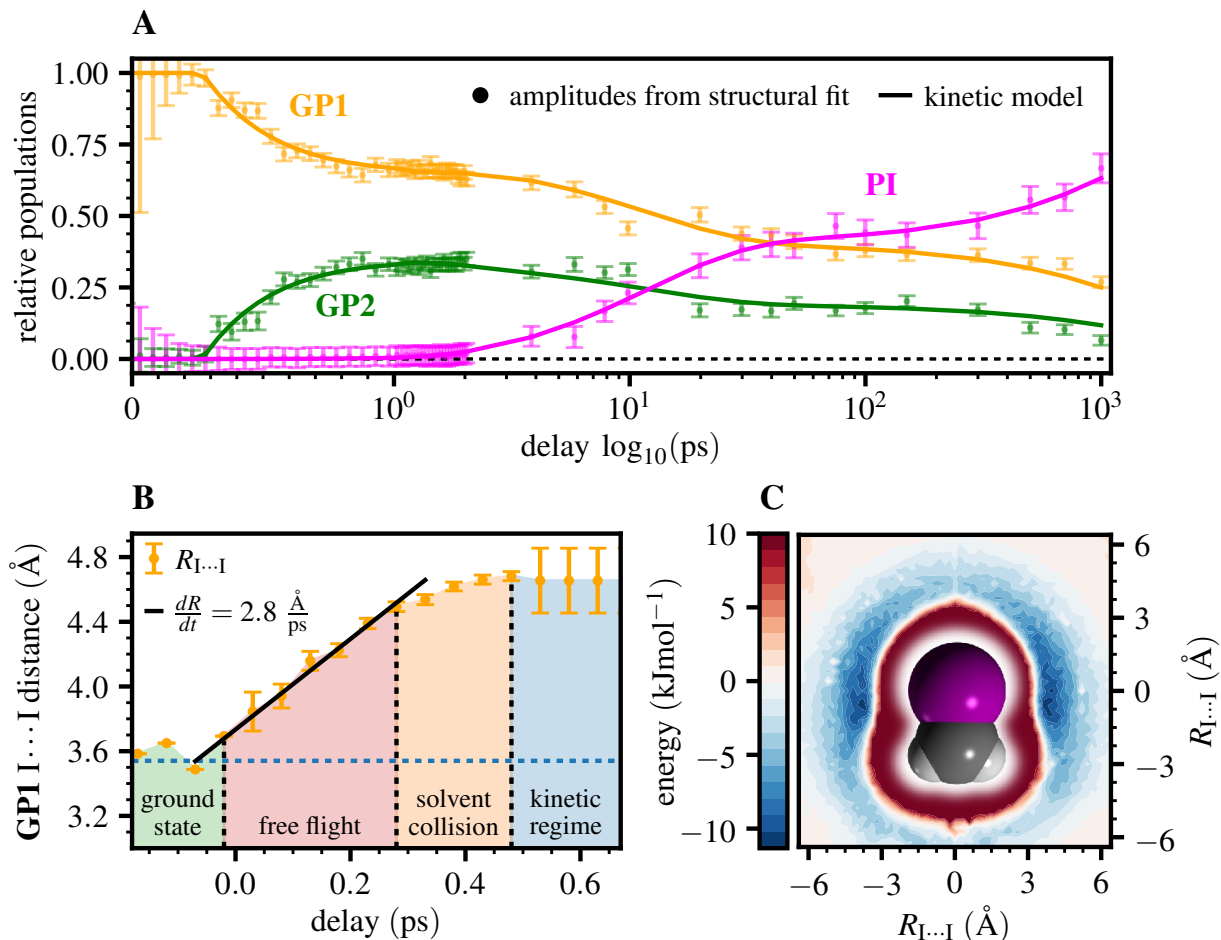


Figure 2: **The incipient I radical velocity is insufficient to break through the solvent cage barrier which reveals long-lived geminate pairs.** Panel A: The dots represent the relative amplitudes of the **GP1**, **GP2**, and **PI** species obtained from the structural modeling (shown in Fig. 1) as a function of delay (ps) after laser excitation. The lines represent a least-squares fit of the numerically integrated rate laws based on the scheme shown in Fig. 3 (see Eq. S16–S22) to the relative populations of iodine-containing species. Panel B: The I $\cdots$ I separation of the **GP1** species as a function of time t . The colored areas separated by dashed lines denote different dynamic regimes. The solid black line is a least-squares linear fit to $R_{\text{I}\cdots\text{I}}$ from -0.07 ps to 0.23 ps. The error bars are hidden for points below and including -0.07 ps. Panel C: Two-dimensional I $\cdots$ I potential energy surface determined by QM calculations. The coordinate (0,0) marks the center of the parent molecule I atom. The I $\cdots$ I distance of the local minimum of the potential energy surface matches the measured I $\cdots$ I separations of **GP1** and **GP2**.

decay concurrently, indicating that these species are in equilibrium. **PI** is formed on the same time scale as the decay of **GP1** and **GP2**, confirming that **PI** is formed from the geminate pairs.

We did not observe any ultrafast formation of the isomer as recently proposed for bromoform in solution (23) and diiodomethane in the gas phase (11).

We cast these observations into a kinetic model (see Eq. S16-S30 in materials and methods (21)) which we fit to the data, the result of which is shown in Fig. 2A. The optimal parameters reveal a biphasic growth of **PI** with characteristic formation times of $\tau_I = 7.7 \pm 0.6$ ps and $\tau_I = 2.0 \pm 0.2$ ns. These values are in good agreement with spectroscopic data obtained under similar experimental conditions (8). The initial rotationally-driven transformation of **GP1** into **GP2** occurs with a lifetime $\tau_r = 0.80 \pm 0.06$ ps, which is approximately twice as fast as predicted by rotational diffusion using the Stoke-Einstein-Debye equation (1.25 ps, see Eq. S14). We consider this to be a consequence of rotational excitation of the $\text{H}_2\text{CI}^\bullet$ fragment after dissociation (7). Curiously, τ_r is longer than the collision time with the solvent (0.25 ps), indicating that rotational energy is not fully dissipated in the first collision with the solvent. This is contrary to what we found for the translational energy and highlights the complexity of solute-solvent interaction under non-equilibrium conditions.

Importantly, the results of our kinetic fit unambiguously show that the radical pair is enclosed in the solvent shell for hundreds of picoseconds. This contradicts the prevailing assumption that a separation of the radical pairs occurs as a result of ballistic solvent-cage escape and diffusion on a picosecond timescale (8, 9, 24). When including structures with $\text{I} \cdots \text{I}$ distances greater than 7 Å in the structural fit, their amplitudes converge to 0. Moreover, the very good performance of the kinetic model (Fig. 2A) strongly suggests that the decay of **GP1** and **GP2** is fully explained by geminate recombination to form **PI**. It was not necessary to include diffusion out of the solvent shell in the model to achieve agreement with the data. Furthermore, the real-space representation of the data in Fig. 2B shows significant populations of **GP1** and **GP2** beyond the maximum measured time delay of 1 ns. Thus, we conclude that the concentration of non-geminate pairs is small for delays ≤ 1 ns.

The long-lived presence of jointly solvated radicals has three important implications. Firstly, the initial kinetic energy of the fragments is apparently insufficient to break through the cyclohexane solvent barrier. This observation is corroborated by the gas-phase dissociation of diiodomethane where only 20% of the available energy is converted into translational energy and the remainder is converted into rotational energy (25). Secondly, a fraction of the radical pairs do not form the **PI** despite their proximity. We can discard the previously proposed loss mechanism where the fragments separate to form non-geminate pairs (NG in Fig. 3) (8). Instead, we propose that the unpaired electrons of a fraction of the geminate radical pairs form a triplet configuration. The triplet configuration inhibits geminate recombination because inter-system crossing must occur preceding **PI** formation. Our proposal is reasonable considering that the photodissociation of diiodomethane leads to a mixture of $\text{I}^\bullet$ radicals in different spin states $\text{I}^*(^2P_{1/2})$ and $\text{I}(^2P_{3/2})$ in the gas phase (25). We assume that a similar excited-state process can occur in solution. Thirdly, an unexpectedly strong interaction must exist between the radical fragments, which keeps them from diffusing into the bulk solvent.

To investigate the inter-radical interaction more thoroughly we performed quantum chemical calculations at the CASSCF-MRCI level of theory. Both the $\text{H}_2\text{CI}^\bullet$ and $\text{I}^\bullet$ fragments are considered in a three-dimensional search space (see materials and methods (21) for details). A two-dimensional energy surface is shown in Fig. 2C for a representative orientation of the $\text{H}_2\text{CI}^\bullet$ fragment with a triplet electronic configuration. As the fragments approach each other from long $\text{I}\cdots\text{I}$ separations, they experience an attractive interaction with a local minimum in the potential energy surface of up to -10 kJ mol^{-1} (blue in Fig. 2C). The attractive interaction envelopes the entire $\text{H}_2\text{CI}^\bullet$ fragment. The potential energy rapidly becomes positive at short $\text{I}\cdots\text{I}$ distances due to Pauli repulsion. MD simulations, parameterized using the results of our CASSCF-MRCI calculations, reveal that the $\sim 4k_{\text{B}}T$ energetic minimum is sufficient to hold the encounter complex in a mutual solvent pocket for hundreds of picoseconds (Fig. S11). The

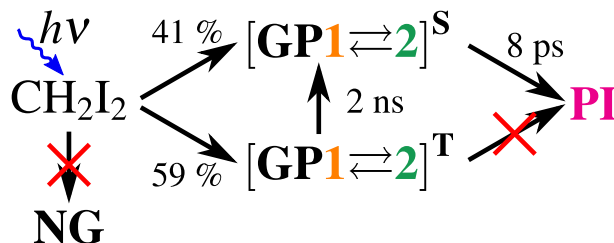


Figure 3: **The mechanism of the photoisomer formation $\text{CH}_2\text{I}-\text{I}$ is revised to include spin states and the spatial configuration of the transient radical encounter complex.** $h\nu$ indicates photo-excitation of CH_2I_2 with a pulse of 266 nm light. **S** and **T** denote the spin-state of the geminate pair. $[\text{GP1} \rightleftharpoons \text{GP2}]^{\text{S}}$ and $[\text{GP1} \rightleftharpoons \text{GP2}]^{\text{T}}$ are shorthand for the equilibrium between the **GP1** and **GP2** radical pairs in the singlet and triplet states, respectively. **NG** stands for non-geminate pairs. The percentage population of the different spin multiplicities, and the lifetimes of the inter-system crossing and isomer formation are noted. Red crosses indicate pathways that do not occur (or do so in negligible quantities).

potential energy minimum is likely caused by dispersion forces, which can be significant in iodine due to its highly polarizable electron cloud. We exclude halogen bonding as a source of the attractive force. This non-covalent interaction is highly directional along the C–I axis and we observe a distribution of $\text{I}^\bullet$ around the $\text{H}_2\text{CI}^\bullet$ fragment. Secondly, previous density functional theory calculations do not predict a significant σ -hole in the similar system CH_3I (26).

The reaction scheme for the photodissociation of CH_2I_2 derived from our data (Fig. 3) illustrates that radical pairs are formed with either a triplet or singlet character. The rotational excitation of the $\text{CH}_2\text{I}^\bullet$ fragment leads to a quick transition of the relative orientation of the fragments (**GP1**→**GP2**). After the initial phase, an equilibrium is established between **GP1** and **GP2**. The singlet species proceed to form the **PI** with a time constant of $\tau_I = 7.7 \pm 0.6$ ps. The triplet species have to undergo spin inversion before isomerization can occur, resulting in the prolonged formation time $\tau_I = 2.0 \pm 0.2$ ns of **PI**. The constituent radicals remain within each others proximity for all probed delay times up to 1 ns due to inter-radical dispersion forces.

The radical pair is the precursor for the isomer formation. We demonstrate here that the spin state of the encounter complex and an attractive interaction between its constituents crit-

ically controls its reactivity. It has been found that the quantum efficiency of alkyl-halogen isomer ($\text{H}_2\text{C}-\text{X}-\text{I}$) formation strongly decreases in the series (27): X = I: 70 %; Br: 49 %; Cl: 9 %. This progression is in line with our proposal that dispersion forces hold the encounter complex together; lighter halogens are less polarizable and hence exhibit weaker dispersion forces. Consequently, the fragments diffuse more easily which decreases the quantum yield of the photoproduct.

Our time-resolved X-ray scattering data directly probe the position and velocity of atoms following the photodissociation reaction. From these data, the existence and properties of the radical encounter pairs were obtained. Although relatively weak, dispersion forces within the encounter complex are critical for the subsequent photo-product formation. Non-covalent interactions have long been known to determine the three-dimensional structure of proteins (28), to control ligand binding in enzymes (29), and to direct self-assembly of supra-molecular structures (30). Here, we show that non-covalent interactions should also be considered in transient encounter complexes of chemical reactions.

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Paper VI

Shedding Light on the Nature of Photoinduced States Formed in a Hydrogen Generating Supramolecular RuPt Photocatalyst by Ultrafast Spectroscopy

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Shedding light on the nature of photoinduced states formed in a hydrogen generating supramolecular RuPt photocatalyst by ultrafast spectroscopy

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ABSTRACT: Photoinduced electronic and structural changes of a hydrogen generating supramolecular RuPt photocatalyst are studied by a combination of by time-resolved photoluminescence, optical transient absorption and x-ray absorption spectroscopy. This work uses the element specificity of x-ray techniques to focus on the interplay between the photophysical and photochemical processes and the associated time scales at the catalytic Pt moiety. We observe a very fast (<30 ps) photoreduction of the Pt^{II} catalytic site, followed by a ~600 ps oxidation step into Pt^{IV}. The latter process is likely induced by oxidative addition of reactive iodine species. The Pt^{IV} species is long-lived and fully recovers into the original ground state complex at a >10 μ s time scale. However, the sensitizing Ru moiety is fully restored at a much faster 300 ns time scale. This reaction scheme implies that we withdraw two electrons from a catalyst that is activated by a single photon.

Introduction

The impact of increasing atmospheric concentrations of CO₂ on life is driving the urgent development of carbon neutral energy conversion approaches. Solar devices are generally considered to be one of the most promising options for environmentally friendly renewable energy. The amount of solar energy reaching the earth in one hour exceeds the annual global energy use¹, illustrating the potential of converting sunlight into electricity or fuel. A key challenge faced in the use of photovoltaic cells lies in the storage of energy. This constraint has stimulated the development of photocatalytic systems that can convert sunlight into fuel directly, with light-driven generation of H₂ from water at the forefront of these efforts.

Amongst various approaches, H₂ generating photocatalysts that mimic photosynthesis have been studied intensively in recent years.^{2–5} In these photocatalysts an organometallic photosensitizer is bound covalently to a catalytic moiety via a bridging ligand (intramolecular approach, see Figure 1). This assembly offers key advantages over an intermolecular approach in which the photosensitizer and catalytic moiety units are mixed in solution, relying on diffusion-limited electron transfer to the catalytic moiety to enable proton reduction.^{6–8} An additional component essential in both approaches is the sacrificial agent, regenerating the photo sensitizer after light-induced electron transfer to the catalytic moiety.

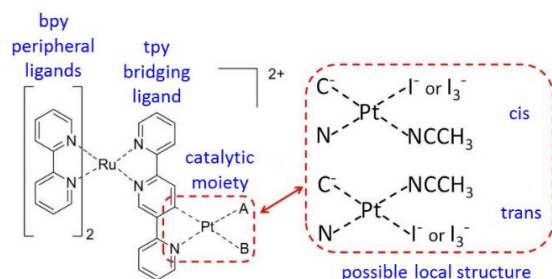


Figure 1. Chemical structure of RuPt in anhydrous acetonitrile.⁹ The right panel illustrates the possible local structures of the Pt catalytic moiety in solution.

Since the first reports on H₂ evolving Ru/M (M = Pd or Pt) organometallic photo-catalysts independently published by Sakai¹⁰ and Rau¹¹ in 2006, efforts have been made to develop efficient supramolecular photocatalysts. To increase their efficiency, control of each of the elementary steps of the overall photocatalytic hydrogen generation process is essential. The mechanistic insights developed here will also be relevant for the economically attractive Cu- and Fe-based alternatives like the recently developed and studied complexes in these references.^{12–18} Many of these successful designs originate from Ru-based photocatalysts. Time-resolved x-ray spectroscopy is a powerful method to achieve mechanistic insight into processes occurring at optically dark catalytic metal moieties and is in the case of light-activated catalysts particularly useful to

detect changes in oxidation state and coordination geometry. It can also be applied to probe the essential electron transfer step to the catalytic site in real-time, and the potential involvement of atomic rearrangements.^{18–22} Experiments at synchrotron facilities typically have a time resolution of tens of ps and are well suited to identify the fast and slow dynamics in complex systems. In addition to visualizing early-time excited state processes, x-ray absorption spectroscopy with μ s time resolution were demonstrated to be capable of tracking reaction intermediates in e.g. the catalytic hydrogen evolution process.^{23–25} These particular experiments were performed on a mixture of a photosensitizer, a sacrificial agent and a Co catalyst (i.e. the intermolecular approach) and allowed to detect the Co^I intermediate species formed by reduction. Importantly, the local structure of the Co catalyst was observed to play a critical role in the transiently formed species and the catalytic activity. These studies illustrate the potential of time-resolved x-ray spectroscopy to develop the mechanistic understanding of the elementary steps involved in photocatalytic hydrogen generation.

We recently reported a series of new Ru-metal photocatalysts, of which the RuPt derivative (see Figure 1) showed a H₂ turnover number of 80 after 6 h of irradiation at 470 nm⁹. An important observation made is that the nature of the catalytic moiety plays a critical role in the early-time photodynamics²⁶, which are generally accepted to have a major impact on the photocatalytic performance.^{27–28} Femtosecond optical transient absorption measurements showed important differences between RuPt and its RuPd analogue.²⁶ The spectro-temporal behavior of RuPt is highly complex, indicating a $\sim$ 1 ps quenching process of the triplet metal-to-ligand charge transfer (³MLCT) states localized on the individual ligands, populated after light absorption and intersystem crossing, by a lower-lying T₃ state. The behavior of RuPt strongly depends on the excitation wavelength, and the contribution of the T₃ state is particularly prevalent for excitation at relatively low photon energies. This T₃ state is unlikely to be localized on the ligands, as it shows a very weak absorption in the blue-ultraviolet region typically associated to ligand-based transitions. The absence of such a $\sim$ 1 ps quenching process for the monomeric Ru precursor suggests that the T₃ state is associated with the Pt catalytic moiety. A second ultrafast process with $\sim$ 100 ps decay time was exclusively observed for RuPt and may thus also be related to the Pt catalytic moiety.²⁶

The minor reduction in ³MLCT lifetime and photoluminescence quantum yield observed for RuPt and its RuPd analogue relative to their monomeric Ru precursor could suggest a photoinduced electron transfer from the bridging ligand to the catalytic moiety at a slow $\sim$ 100 ns time scale^{9, 29}. An alternative explanation is that the photoluminescence intensities and lifetimes may reflect relative populations of excited states localized at the individual ligands (with the state at the bridge potentially delocalized over the catalytic moiety²⁹), rather than the dynamics of intramolecular electron transfer from the photosensitizer to the

Pt. Thus, the photoexcited electron density in the complex may become delocalized over the bridging ligand and the Pt catalyst much faster than these photoluminescence data suggest. To discriminate between these two scenarios, synchrotron-based transient x-ray absorption experiments with ps time resolution have been pursued to identify photoinduced changes in oxidation state and the geometry of the Pt catalytic moiety. The interpretation of the time-resolved x-ray absorption data is supported by transient optical absorption and photoluminescence data.

In the ground state Pt is in its 2+ oxidation state, as Pt^I species are unstable.³⁰ Pt^{II} has a d8 configuration and is well-known to form a square-planar coordination complex.³¹ As shown in Figure 1, Pt is coordinated to one C atom, one N atom and two I atoms.^{9, 32} Upon dissolving in acetonitrile, one solvent molecule likely becomes coordinated to the Pt atom, substituting one I⁻ anion.^{9, 32} The fourth coordination site likely remains occupied by an I⁻ anion, as indicated by NMR and elementary analysis.⁹ The position of the I⁻ anion and the solvent molecule may adopt either a cis or a trans configuration (see Figure 1). A number of photochemical reactions involving the bound and the now free I⁻ ions are feasible, such as the formation of I₃⁻ at the I⁻ coordination site, or the reaction of Pt with I₂ or I₂⁻ in an oxidative addition process forming a hexa-coordinated Pt complex.³³⁻³⁵

The aim of this study on RuPt is thus to shed light on the nature of the optically dark T₃ state and understand the photochemical processes at the Pt catalytic moiety.

Experimental section

Synthesis and steady-state optical characterization

The synthesis of RuPt with this bridging structure can lead to the formation of a di-nuclear form with one Ru sensitizing moiety and one Pt reaction center or to a penta-nuclear form with two sensitizer and three connected Pt atoms as described in detail in ref. 9. The current experiments were performed on the di-nuclear structure shown in Figure 1. The complexes were dissolved in acetonitrile (Sigma-Aldrich, anhydrous, purity >99.9 %) and placed in 1 cm path length cuvettes for steady-state optical measurements. UV-vis absorption spectra were recorded using a Shimadzu UV-1800 spectrophotometer. Steady-state photoluminescence spectra were obtained using a Horiba Jobin Yvon FluoroMax-4 spectrofluorometer with excitation at 450 nm. Both absorption and photoluminescence spectra were recorded at room temperature.

Time-resolved optical experiments

Transient absorption experiments were both pursued in the fs-ps time window and the ns-μs time window. The polarization of pump and probe was set at 54.7° to avoid anisotropy effects. The fs transient absorption (TA) setup²⁹ and experimental conditions²⁶ were described in detail earlier.

The ns TA experiments were performed with a frequency-doubled electronically delayed and triggered

Nd:YVO₄ laser with 3 mJ/cm², 1 ns, 532 nm as the pump and a supercontinuum probe generated by focusing 800 nm, 65 fs laser pulses into a CaF₂ crystal. The CaF₂ crystal was mounted on a continuously moving stage to avoid thermal damage. The supercontinuum probe signal was dispersed by a grating and measured with a pair of diode arrays. The sample was dissolved to 0.02 mM in anhydrous acetonitrile (Sigma-Aldrich, purity >99.9 %), degassed by dry Ar for 15 minutes and sealed in an airtight 1 mm cuvette.

Photoluminescence decays were obtained by exciting the RuPt sample (0.02 mM in anhydrous acetonitrile, Sigma-Aldrich, purity >99.9 %, degassed by dry N₂ for 30 minutes) with the frequency-doubled output of a Nd-YAG laser (532 nm). The photoluminescence signal was dispersed by a spectrograph and detected using an amplified CCD camera. The signal acquisition by the camera was gated electronically. The photoluminescence decay was obtained by integrating the recorded emission signal in a spectral window from 550 nm to 820 nm at various gate delays. The full width at half maximum of the instrumental response function (Gaussian) was determined to be 4.7±0.2 ns. The data were corrected by subtracting the background dark counts.

Steady-state X-ray absorption experiments

Steady-state x-ray absorption spectra of the Pt L₃ edge in the near-edge (XANES) and extended (EXAFS) regime were obtained at the beamline 11-ID-D of the Advanced Photon Source (Argonne, IL, USA) during the same measurement campaign as the transient x-ray spectra discussed below. The RuPt photocatalyst was dissolved in 75-100 ml batches to a concentration of 0.5 mM - 1 mM in anhydrous acetonitrile (Sigma-Aldrich, purity >99.9 %), degassed by dry N₂ for 30 minutes and kept under constant N₂ environment during the measurement. The solution was flown in a round jet with approximately 1 mm diameter and a flow speed of 1-2 m/s. The total x-ray induced fluorescence was measured by two x-ray diodes equipped with Soller slits and a Z-1 Zn foil of 6 absorption lengths. Details of the setup were reported earlier.³⁶ The energy was calibrated simultaneously by measuring the x-ray absorption spectra of a metallic Pt foil using the x-ray photons after the sample jet.

Due to the collection mode described in the next section, the steady-state near-edge spectra were collected continuously during the whole experimental campaign, allowing the intervention once the first accumulative sample damage was observed, typically after 16 h - 18 h of data collection. These XANES were collected by using bunches that probe a fresh section of the jet, long after the section excited by the pump light left the probe area but before the following pump pulse arrives. During data analysis the spectra were filtered and no data was used in which any (integrated) sample damage was significant. The damaged sample shows a distinct differential feature very different from the two pump-probe signals shown below. The below described mode of data collection ensured that the steady-

state XANES was collected with significantly higher statistics (approx. $\times 4000$ times) than the single bunch synchronous pump-probe experiment for the same time interval. The whole sample volume was illuminated in less than 4 minutes. This procedure also ensured the observation of accumulative chemical reaction(s) altering the XANES spectra, if occurring.

Time-resolved X-ray absorption experiments

Time-resolved x-ray absorption measurements were pursued at beamline U-D-D of the Advanced Photon Source (Argonne, IL, USA). Details of the experimental setup were described in the previous section and in earlier publications.³⁶ The experiments were conducted in the 24 bunch mode with a bunch separation of 153 ns and a typical x-ray bunch width (FWHM) of 79 ps. The sample was excited with a 527 nm laser pulse of 5 ps duration focused to a 500 μm diameter spot size with $\approx 190 \text{ mJ}/\text{cm}^2$ per pulse and 1.6 kHz repetition rate. The excited spot on the flowing liquid jet was probed with the synchronized x-ray bunch at the chosen time delay after laser excitation and the consecutive bunches were spaced in 153 ns time intervals. The bunch-to-bunch normalization allowed the use of the same x-ray bunch during multiple orbits in the storage ring and thus the study of dynamics beyond 3.6 μs with the same photoexcitation pulse. After approximately 320 μs , the laser irradiation area flew completely out of the probed region (as evidenced by following a linear decaying signal and verified by estimations based on flow speed and laser focus area) and a number of bunches were used to collect steady-state XANES before the arrival of the next laser pump pulse, which was thus exciting a fully refreshed sample spot. The probing x-ray spot was with approximately 50 μm (vertical) by 500 μm (horizontal), significantly smaller than the pump and it is thus reasonable to assume a homogeneously excited sample. From the steady-state optical absorption, geometry and pump light photon flux, 2.3 % of the molecules in the probed spot were estimated to be photoexcited.

Data analysis

The open source program Glotaran³⁷ was used for analysis of the fs-ps transient absorption data. The ns optical data was analyzed using methods provided by the python computational package SciPy³⁸ and a newly developed python based analysis suite. The data of multiple scans was averaged, sections that showed scattered light from the pump beam were masked and the data was binned into equal 1 nm wavelength bins. The data was then modelled with consecutive exponential decays using a 1 ns instrument response function and a global analysis scheme presented previously.³⁹⁻⁴¹ In short, a model is formed that predicts the temporal development of different species using the lifetime parameter as input. For each new set of lifetime parameters the spectral components are assigned to each species by a least-mean-square optimization to the data. A Nelder-Mead minimization algorithm from the

SciPy computational package is used to minimize the χ^2 by optimizing the lifetime parameter for the given model, the instrument response function and potential time-offsets. The decoupled optimization of lifetime parameter and spectral components makes this type of analysis robust against noise in the measured transient spectra.

Steady-state EXAFS were analyzed using the Athena and Artemis packages⁴². The scattering paths were calculated using FEFF 6. The analysis followed the approach recommended in the literature.⁴³⁻⁴⁴ The absolute energy scale of each scan was calibrated with a simultaneously collected reference foil measurement. The parameter of the model were optimized both in k and R space with k , k^2 and k^3 weights, leading to fits of very similar quality. Different model molecules were generated with a procedural code and their parameter in turn refined in Artemis. In addition to this parameter refinement, a number of other structural models were tested by calculating the full multiple scattering with FEFF 8.6⁴⁵ and generating/optimizing these structure with a procedural code followed again by an EXAFS refinement. This second procedure was necessary to test a wider range of possible structural alternatives as the simple refinement method permitted.

The XANES scans were energy calibrated using the reference foil, scaled to an edge step of one and summarised for a number of different bunches of the probing x-ray light. This averaged data was compared for different periods of one sample batch and between different sample batches to exclude data from radiation damaged molecules. Once radiation damage was observed, data from this batch was excluded from the analysis. The transient XANES for delay times $< 2 \text{ ns}$, 150 ns and 300 ns was formed by averaging the signal of single bunches following laser excitation. The transient data for longer delay times uses the average of multiple consecutive x-ray bunches (spaced by 153 ns).

For modelling of the XANES at the L_3 edge, a new python routine was created that combines parametric movement (translation and rotation) of single atoms or whole structural groups with control parameters describing e.g. the electronic configuration and other calculation parameter into input files for FEFF9 or similar codes.⁴⁵ This routine handles the output of FEFF9 and thus enables the efficient and restrained optimization of all parameter or, limiting the number of FEFF runs, the optimization on a surface span by a variation of parameter similar to the approach in FitIt⁴⁶. By using this method, a wide variety of structures and parameters were created, allowing to calculate the XANES and compare these to the experimental spectra. The linear regression was done using the SciPy Statsmodels package.⁴⁷

Results and discussion

Absorption and fluorescence properties

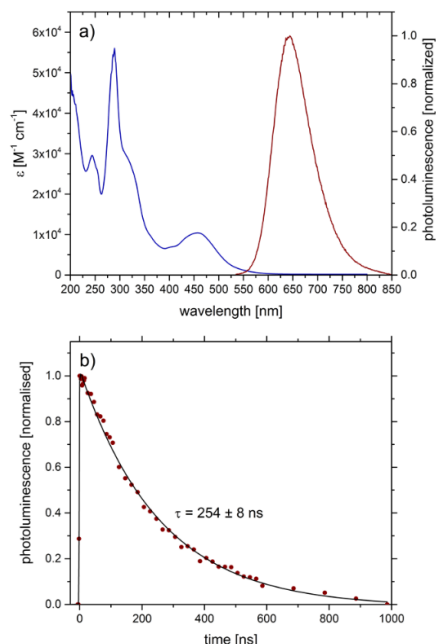


Figure 2. (a) Optical extinction coefficient (blue) and photoluminescence spectra (red) of RuPt in anhydrous acetonitrile and (b) photoluminescence decay integrated from 550 nm to 820 nm obtained at 532 nm excitation (red points), including a fit to a mono-exponential decay function and the resulting lifetime.

Figure 2a shows the steady-state absorption and photoluminescence spectra of RuPt. The sharp absorption band at ca. 289 nm is likely due to ligand-centered (LC) $\pi-\pi^*$ transitions of the peripheral bpy ligands, and the shoulder around 320 nm due to LC $\pi-\pi^*$ transitions of the bridging 2,2':5,2''-terpyridine (tpy) ligand. The broad absorption band centered at 457 nm likely originates from Ru-based singlet metal-to-ligand charge transfer ($^1\text{MLCT}$) transitions to the bpy and tpy ligands.^{9, 26} As intersystem crossing is expected to occur very fast in these type of complexes (<100 fs)⁴⁸⁻⁴⁹, the photoluminescence centered at 644 nm is indicative for radiative relaxation from a manifold of lowest $^3\text{MLCT}$ states to the ground state.²⁸⁻²⁹ The photoluminescence decay has been measured for photoexcitation at 532 nm. Figure 2b shows the photoluminescence decay integrated over nearly the entire emission band from 550 nm to 820 nm due to the low molar absorptivity at 532 nm resulting in a weak signal. The decay is well described by a mono-exponential decay function with a lifetime of 254 ± 8 ns.

Transient optical absorption

To support the interpretation of the time-resolved x-ray absorption data discussed below, transient absorption experiments have been pursued at various pump wavelengths and time windows. Figure 3a shows the fs transient absorption spectra of RuPt at 527 nm excitation, with a strong excited state absorption (ESA) band >530 nm indicating population of the T_3 state.²⁶ The negative signal from 450 nm - 520 nm is due to ground state bleach (GSB). The weak ESA in the 350 nm - 450 nm window suggests a minor

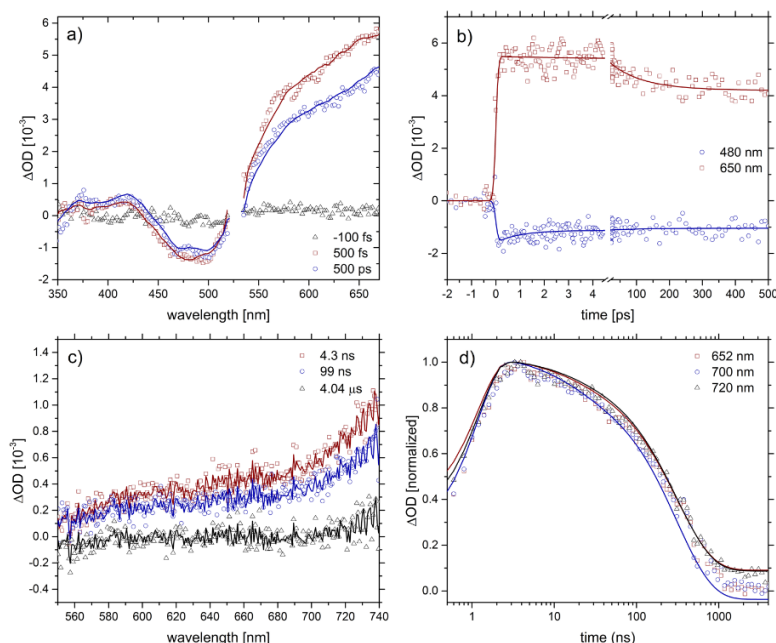


Figure 3. (a) Femtosecond transient absorption spectra of RuPt in anhydrous acetonitrile at 527 nm excitation and (b) kinetic traces at key wavelengths, with fits based on a sequential model with lifetimes of 980 ± 184 fs and 99 ± 12 ps included as lines. (c) Nanosecond transient absorption spectra at 532 nm excitation and (d) kinetic traces at key wavelengths with fits based on a sequential model with lifetimes of 21 ± 5 ns and 340 ± 50 ns included as lines. The signal raise corresponds to the 1 ns pulse width of excitation light.

population of the $^3\text{MLCT}$ states.²⁶ Figure 3b shows the kinetic traces at 480 nm and 650 nm. The signal at 480 nm becomes less negative on a ~ 1 ps time scale, indicating a potential $^3\text{MLCT} \rightarrow \text{T}_3$ quenching process which is more evident for excitation at higher photon energies.²⁶ Photoexcitation at 516 nm or 480 nm (favoring the population of $^3\text{MLCT}$ states) also gave a third kinetic component indicating ~ 5 ps $^3\text{MLCT}_{\text{bpy}} \rightarrow ^3\text{MLCT}_{\text{tpy}}$ internal conversion competing with vibrational cooling at the bpy ligands. The lack of evidence for this process at 527 nm photoexcitation with the simultaneously strong ESA for the T_3 indicates a non-equilibrated population of excited states between the ligands and a favored population of the T_3 state due to lower excess photoexcitation energy. The broad ESA >550 nm partially decays on a ~ 100 ps time scale, as illustrated by the kinetic trace at 650 nm. The nature of the T_3 state is unknown, although the absence of the ~ 1 ps and the ~ 100 ps components for the Ru monomeric precursor and the RuPd analogue²⁶ seems to suggest an important role of the Pt catalytic moiety. As discussed in the introduction, it is unclear when the photoelectron reaches the Pt moiety and what the nature of electron transfer is.

Transient optical absorption experiments have also been performed in the ns – μs time window (Figures 3c and 3d, photoexcitation at 532 nm). Analogous to the early-time spectra shown in Figure 3a, a strong ESA >550 nm is observed. Its spectro-temporal behavior is well described by two time scales of 21 ± 5 ns and 340 ± 50 ns. The latter value is relatively close to the photoluminescence lifetime (Figure 2b), the difference in values may be due to different experimental conditions, in particular the photoexcitation intensity, concentration and degassing conditions. The normalized kinetic traces in Figure 3d show that the decay is independent of the ESA wavelength in the probed range. The origin of the 21 ± 5 ns and 340 ± 50 ns decay times will be discussed below.

Steady-state x-ray absorption

Figure 4 shows the analysis of the steady-state extended x-ray absorption fine structure (EXAFS) data. The measured EXAFS was fitted to a number of different structures, including amongst other the original RuPt photocatalyst and the complex in which one or both I^- anions were replaced by acetonitrile or I_3^- (see the ESI for a complete list). For each structure the parameters were optimized to yield the best χ^2 and the resulting structural parameters were analyzed for feasibility (results with e.g. negative Debye-Waller factors were rejected). In the optimum χ^2 associated structural configuration one I^- anion is replaced by acetonitrile in the cis configuration (see Figure 1). The right panel of Figure 4 presents this optimized structure and its parameters, confirming earlier calculated parameters except for a slightly extended Pt-N1 bond length (1.968 ± 0.01 Å vs 2.1 Å).^{9, 29} This structure was used as the basis for all further calculations.

Transient x-ray absorption

The earliest difference absorption spectrum at 30 ps (Figure 5c) indicates that the Pt catalyst is already reduced at this time scale. The linear regression analysis, i.e. $\log_e(\text{intensity})$ vs. time presented in Figure 5b, shows that the signal intensity decreases on a 930 ± 100 ps timescale. The change in shape of the integrated signal suggests that this decay is due to more than a single component. Thus, a singular value analysis (SVD) was pursued to elucidate the involvement of different spectral components. Figures 5d-f shows the results of this analysis, in which the data matrix M , which represents spectra corresponding to different delays, was factorized into $M = USV^*$. The first two spectral components in U have significant features and are shown in Figure 5f, scaled with the singular values from S whose values are drawn in Figure 5d. These two spectral components have the same shape as the measured spectra at 60

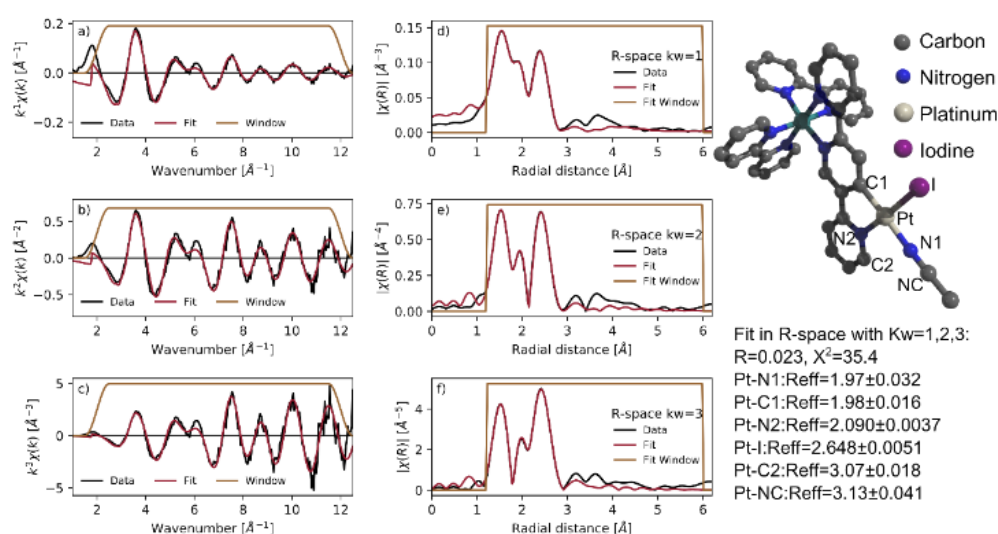


Figure 4. Analysis of extended x-ray absorption fine structure spectrum. Panels (a-c) present the data and fit in k-space for different k-weights, panels (d-f) are data and window in R-space for different k-weights. The fit was performed in R-space with $k_w = 1, 2, 3$ and paths up to 3.2 Å. The key results and structure are shown in the right panel with distances given in Å.

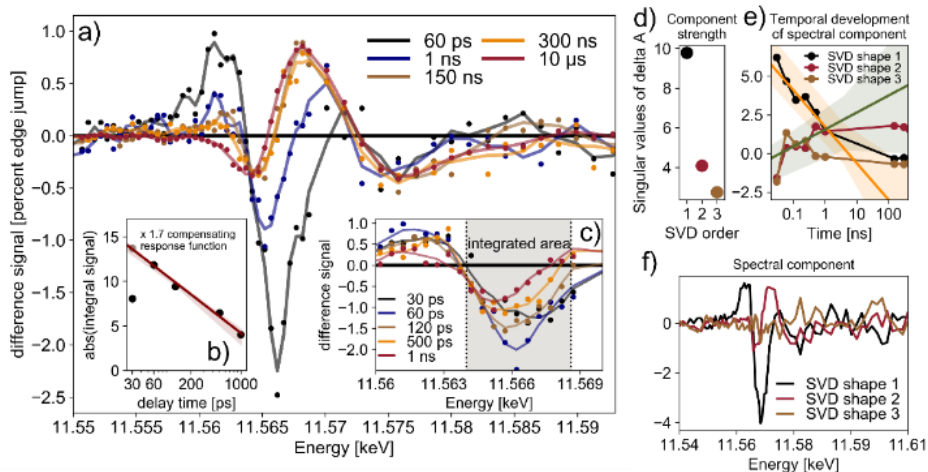


Figure 5. a) Transient x-ray absorption spectra of RuPt in anhydrous acetonitrile at various time delays after 527 nm photoexcitation (dots, the lines are intended to guide the eye). c) Zoom-in around the Pt L₃ absorption edge at early time scales, b) signal intensity integrated over the grey area in c). The linear regression (without the 30 ps point) suggests a lifetime of 930 ± 100 ps. The time point at 30 ps is also shown corrected for the partial overlap of x-ray pulse and pump pulse. d)-f) singular value decomposition (SVD) analysis of the signal matrix. d) The total intensity of the selected SVD component. e) The temporal evolution of the first three spectral components shown in f). The linear regression (without the 30 ps time point) suggests a lifetime of 880 ± 117 ps for SVD component 1 and 630 ± 270 ps for SVD component 2 (see text).

ps and 10 μ s (see Figure 5a) and their time-evolution is thus relevant and can be analyzed. The small S value, spectral shape and unphysical time evolution of the third spectral vector suggests that it has to be considered as primarily noise related. The temporal evolution of the first two vectors were again modelled by linear regression (without the 30 ps time point, using only the time points up to 1 ns), suggesting a lifetime of 880 ± 117 ps for SVD component 1 and 630 ± 270 ps for SVD component 2. The lifetime for the first component and the value determined from the integral in Figure 5b (930 ± 100 ps) match within the error margins. It is visible that synchronous to the decay of the first spectral component, the growth of the second spectral component halts and is stable within this time window. There are minor changes between the spectra measured at 150 ns and 300 ns, as well as between the spectra measured at 300 ns and 10 μ s (see Figure 5a). The first spectral component has no intensity left at these measurement times.

The XANES spectra were modelled using the software package FEFF 9.6.⁵⁰ with the self-consistent field potentials and multiple scattering algorithm (full parameter set is given in the ESI). In Figure 6a the measured ground state XANES (brown) is shown versus the modelled ground state (black, abbreviated **GS**). The ground state model **GS** reproduces the measured spectrum very well, including the position of the features at 11.575 keV and 11.585 keV, while slightly underestimating the total intensity in this region. This behavior has also been found in other publications.⁵⁰⁻⁵¹

To model the reduced state (**RS**) we have taken into account the higher occupancy of d level (shift of Fermi level by 1 eV) accompanied by small chemical shift of the spectrum (0.3 eV), keeping the same local structure of the complex. It describes the difference spectra measured at 60 ps

well (see Figure 6b). The SVD analysis indicates that the transient at 60 ps is a mixture, with ca. 86 % **RS** and 14 % of the species dominant at 10 μ s. This mixed model describes the shape at 11.568 keV better than the pure **RS** model.

The long-lived species which is observed for delay time 10 μ s is characterized by a higher intensity of the white line (positive transient signal at 11.568 keV) and shift of the absorption edge to higher energies (negative signal at the rising edge of the spectrum around 11.564) (Figure 5a). These are the typical signatures of Pt oxidation suggesting a long-lived Pt^{IV} intermediate. To understand the origin of such an intermediate it is important to point out that during the initial solvation, each RuPt complex releases one I⁻ ion as can be understood by the difference between crystal structure and the solvated structure discussed above. Thus a large number of I⁻ ions are available in solution and two processes may occur. The first one is the formation of I₃⁻, followed by the substitution of I⁻ by I₃⁻. We have explored the formation of I₃⁻ by time-resolved Raman at 255 nm to detect the characteristic I₃⁻ lines and did not observe a signal enhancement. A second process suggested in the literature, combining a strong oxidation with an enhancement of the white line, is oxidative addition.³³⁻³⁵ Here I₂ from the solution oxidizes the complex into a hexa-coordinated Pt^{IV} species. We do have a significant amount of I⁻ ions present and it is thus likely that I₂ is formed and this process is possible.

The strong oxidation, observed experimentally as the white line enhancement and the failure to observe the characteristic I₃ Raman signatures suggest that this is indeed the more likely process of the two. We have thus modelled the observed oxidative process at 10 μ s with the hexa-coordinated Pt species shown in Figure 6c (abbreviated as **HP**)

which shows reasonable agreement with the experiment. Alternative models with different combinations of all components available in solution occupying different bonding sites at various distances and angles give worse agreement with the experimental data (see SI).

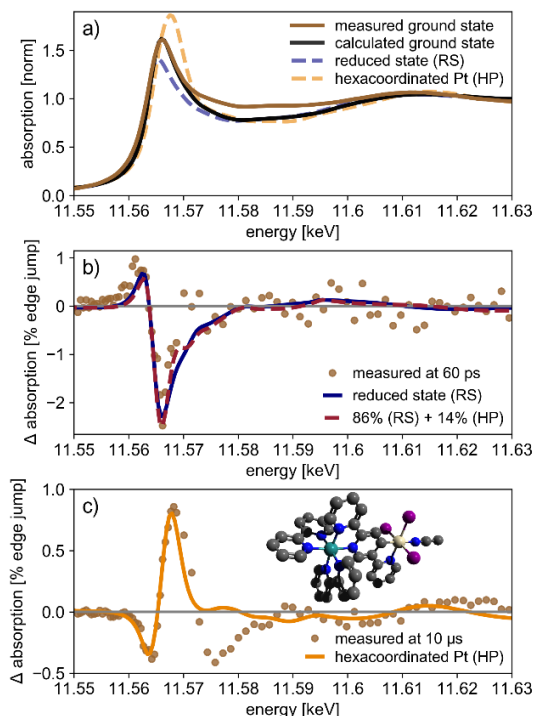


Figure 6. Modelling of XANES data: a) measured ground state spectrum (brown) compared to the calculated ground state spectrum (black) and two excited states RS and HP, b) difference XANES measured at 60 ps delay modelled with a reduction of the Pt^{II} site (RS) and a linear combination of RS and HP, c) difference spectrum at 10 μs (brown), modelled with an oxidative addition of two iodine ions (HP). The inset shows the modelled complex.

Discussion

The population of $^1\text{MLCT}$, $^3\text{MLCT}_{\text{bpy}}$, $^3\text{MLCT}_{\text{tpy}}$ and T_3 states depends on the photoexcitation wavelength and is non-equilibrated. More excess energy leads to a larger population of $^3\text{MLCT}_{\text{bpy}}$ and $^3\text{MLCT}_{\text{tpy}}$ states, and more ~ 5 ps $^3\text{MLCT}_{\text{bpy}} \rightarrow ^3\text{MLCT}_{\text{tpy}}$ internal conversion competing with vibrational cooling at the bpy ligands. The excitation wavelengths used in this work (527 nm and 532 nm) favor ultrafast population of the T_3 state. The fs transient optical absorption data indicate that this state is also populated via a ~ 1 ps $^3\text{MLCT} \rightarrow T_3$ quenching process (Figures 3a and b). The earliest difference x-ray absorption spectrum at 30 ps (Figure 5c) already shows the reduction of the Pt site. Hence, ultrafast population of the T_3 state may correspond to reduction of Pt^{II} into Pt^{I} .

The subsequent time scale observed by transient optical absorption is ~ 100 ps. The absence of a strong ~ 100 ps component in the x-ray data indicates that this process is not directly correlated to the Pt moiety. The 40-50 ps rotational time of $[\text{Ru}(\text{bpy})_3]^{2+}$ in acetonitrile at room temperature observed earlier⁵²⁻⁵³ suggests this component to be due to a change in orientation of the RuPt photocatalyst.

From the time evolution of the ΔXAS , we observe first a prompt appearance of a species with the signature of reduced Pt which decays on a 930 ± 100 ps time scale (Figure 5b and e). The ΔXAS evolves in both shape and magnitude into the spectrum measured at 10 μs , indicating that a strongly oxidized species is formed on a 630 ± 270 ps time-scale, which has a lifetime $> 10 \mu\text{s}$. The formation of the second species does not progress after decay of the reduced species, showing that reduction of Pt is essential for this reaction. The two timescales are different as is the intensity of the signal. This does suggest two separate decay paths from the reduced Pt^{I} state.

Based on these arguments, we suggest that the strong oxidation process is oxidative addition of I_2 to Pt forming a hexa-coordinated Pt^{IV} complex.³³⁻³⁵ The reduced amplitude of the difference signal (despite the strong oxidation) and the slower decay rate of the initiating species suggest additional rate-limiting processes, maybe related to I_2 .

The large error bars of the time scales make this argumentation however a mere suggestion that needs to be verified by additional experiments, such as x-ray studies using the iodine edge. The general time scale of < 1 ns for the oxidation reaction is very short, which could suggest a prior arrangement of the reacting species.

The 21 ± 5 ns and 340 ± 50 ns components observed by transient absorption (Figure 3d) and the 254 ± 8 ns photoluminescence decay (Figure 2b) are nearly absent in the x-ray data, which only show a minor change between 150 ns and 300 ns, and 300 ns and 10 μs . The latter difference is already present at 450 ns (data not shown). The absence of a significant change in x-ray spectra suggests these processes to be associated with the Ru moiety rather than the Pt catalyst. The full ground state recovery (Figure 3d) also indicates that the electron that originally reduced the Pt moiety has either returned or is replaced from the solvent. We cannot distinguish between the pathways leading to ground state recovery at the Ru moiety and thus have tentatively labelled the species differently. Figure 7 shows a Jablonski diagram of the proposed photoinduced processes.

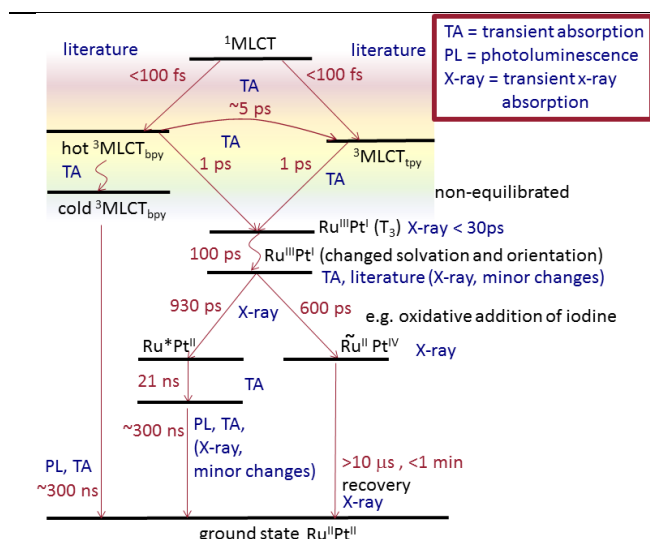


Figure 7. Jablonski diagram of processes occurring after photoexcitation of RuPt, with the technique supporting this conclusion indicated.

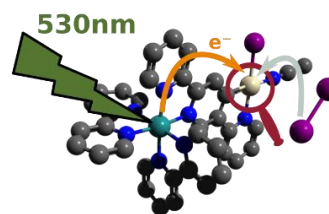
The likely involvement of reactive iodine species (i.e. I^- , I_3^- and/or I_2) in the strong oxidation process following the photoinduced reduction of Pt^{II} into Pt^{I} may have important consequences for the mechanism of H_2 generation. The state-of-the-art design principle of supramolecular photocatalysts is based on the use of more photons (two for H_2 generation⁵⁴) and requires accumulative charge separation.⁵⁵ We activate this catalyst with a single photon but withdraw two electrons from the Pt. Such an approach could thus potentially bypass the need for the highly challenging charge accumulation and should be investigated in more detail under catalytic conditions. This mechanism might also explain the generally higher photocatalytic activity of iodine-based photocatalysts relative to e.g. chloride alternatives^{56–57} and presents a novel paradigm for hydrogen generation by supramolecular photocatalysts.

Conclusion

In summary, transient optical and x-ray absorption spectroscopy studies on light-induced electronic and structural changes of a hydrogen generating supramolecular RuPt photocatalyst show that reduction of the Pt catalyst occurs at an ultrafast <30 ps timescale. The population of excited states is non-equilibrated at early times (<5 ps) and vibrational relaxation is competing with internal conversion towards the bridging ligand and the catalyst. Thus, not every absorbed photon leads to reduction of the Pt catalyst. The reduced intermediate species decays at a sub-ns time scale via two processes; a part of the complexes are strongly oxidized while a second part is returning to the ground state. The strong oxidation process may be driven by oxidative addition of reactive iodine species. The formed intermediate is long-lived ($>10 \mu\text{s}$) and ultimately recovers into the original ground state. The catalyst is activated by a single photon and the potential involvement of the I_3^-/I^- redox

couple may bypass the need for accumulative charge separation in H_2 generation.

Graphical Abstract



ASSOCIATED CONTENT

ESI attached

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Present Addresses

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Paper VII

Ultrafast X-ray scattering measurements of coherent structural dynamics on the ground-state potential energy surface of the Pt_2POP_4 molecule

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Ultrafast X-ray scattering measurements of coherent structural dynamics on the ground-state potential energy surface of a diplatinum molecule

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Here we report XFEL experiments addressing the ground-state structural dynamics of the di-platinum anion Pt_2POP_4 following photoexcitation. Off-resonance excitation is used to prepare a vibrationally cold excited-state population complemented by a structure-dependent depletion of the ground-state population. The structural dynamics are tracked with <100 femtosecond time resolution by X-ray scattering, utilizing the anisotropic component ($\Delta S_2(Q, t)$) to suppress contributions from the bulk solvent. The X-ray data exhibits a strong, long-lived oscillatory pattern and structural analysis shows this as arising from dynamics of the Pt-Pt bond length with period $T = 0.284(1)$ ps and lifetime $\tau = 2.2(2)$ ps. The results are compared with QM/MM simulations of the off-resonance excitation and the subsequent evolution of both excited- and ground-state sub-populations.^a

Optical laser systems with pulse lengths down to the single-femtosecond regime has enabled a host of studies of the excited-state kinetics and dynamics in a very wide range of systems [1, 2] and with the arrival of X-ray and electron sources with pulse lengths in the sub-picosecond regime, the bond-length and -angle dynamics of the photoexcited molecules can now be directly measured [3–8]. However, the majority of chemical reactions take place between molecular species in their electronic ground states and the energy landscape of ground-state molecules is therefore of fundamental interest. The vibrational level spacing of these states can be probed via steady-state IR or Raman spectroscopic methods. The dynamics of ground-state molecules have mainly been investigated through time-resolved methods based on preparing non-equilibrium, coherent vibrational states through combined absorption and Raman processes involving an excited-state potential surface. Such spectroscopy is today a highly mature field spanning several similar but distinct methodologies, e.g. Resonant Impulsive Stimulated Raman Scattering (RISRS) and Coherent Anti-Stokes Raman scattering (CARS) [9–14]. These advanced spectroscopy methods provide a powerful approach to characterizing vibrational eigenfrequencies for harmonic modes, but do not directly access bond

lengths and angles. Therefore the information about the underlying structural dynamics of the nuclei has to be inferred from the observed frequencies, utilizing phenomenological structure-energy relationships or by comparison with simulations. Similar limitations apply to the so-called *Lochfrass* or ‘*R*-dependent ionization’ spectroscopies, where the ground state is selectively depleted as a function of some key structural parameter [15–19].

The reliance on indirect, albeit powerful, spectroscopic methods to probe the potential energy landscape of ground-state molecules has been due to a lack of structurally-sensitive probes with the requisite sub-picosecond time resolution. In this work we show how exceptionally brilliant hard X-ray Free Electron Laser (XFEL) sources [20] now make it possible to directly map, in real-time, the structural dynamics of an ensemble of molecules as it evolves on the ground-state potential surface and interacts with the surrounding solvent molecules. As an illustration of this approach we investigate how the ground-state population of the much-studied di-platinum anion PtPOP $[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]^{4-}$ (Figure 1) [21–30] evolves in real-time following d_{PtPt} -dependent photo-depletion of the ground state population. The results of the structural analysis of the X-ray data are directly compared with quantum mechanics/molecular mechanics (QM/MM) Born-Oppenheimer Molecular Dynamics (BOMD) simulations [31, 32] of the dynamics.

The photophysics of PtPOP have been studied for almost four decades [30] and it is very well established

^a Abstract is also still a few characters too long. Limit is 600 characters, but based on the CoTerpy article it is not too strictly enforced.

that optical excitation in the absorption band centered at 370 nm promotes an electron from the anti-bonding $5d\sigma^*$ HOMO orbital to the bonding $6p\sigma$ LUMO orbital [22]. As the $p\sigma$ orbital is located between the two Pt atoms, such excitation leads to a contraction of the Pt atoms along the Pt-Pt axis, changing the molecular structure from having an equilibrium Pt-Pt distance of $d_{\text{PtPt}}^{gs} = 2.9$ - 3.0 Å to having an excited-state Pt-Pt distance of $d_{\text{PtPt}}^{es} = 2.7$ - 2.8 Å. This structural change has been directly measured both in the crystal phase [23, 24] and in solution [25, 26].

The properties and dynamics of the initially excited singlet electronic state and the long-lived (lifetime $\tau \sim 10$ μs), chemically reactive and strongly luminescent triplet excited state have recently been investigated in great detail using optical spectroscopy [27, 29]. Figure 1 shows in schematic form the potential surfaces of the ground- and excited state, the shape of which determine the structural dynamics following photoexcitation. The offset in equilibrium Pt-Pt distance between the ground and excited states is significant, and excitation around $\lambda = 370$ nm leads to very well-defined and highly harmonic oscillations with period $T^{es} = 0.23$ ps / 0.21 ps (singlet/triplet, [29]) in the UV-VIS spectra. These oscillations have been assigned to Pt-Pt oscillations and remain coherent for several picoseconds after the photoexcitation event with decay time $\tau = 1.7$ - 3 ps in aqueous solution [27, 29].

Regarding the ground state potential surfaces, early low-temperature optical spectroscopy in the crystal phase [22] and Raman spectroscopy in solution [33, 34] determined the ground-state potential to be also highly harmonic but slightly softer than the singlet- and triplet-state potentials with a Pt-Pt oscillation frequency having period $T^{gs} = 285$ fs. Much effort has been devoted towards investigating the energy dissipation mechanisms and structural dynamics of the excited-state structure(s) of PtPOP also in recent years [35–37], but few or no studies have addressed the ground-state dynamics of PtPOP along such lines.

To directly investigate the ground-state dynamics of PtPOP, off-resonance optical excitation at 395 nm is here utilized to create a hole in the ground state population by selectively exciting solute molecules at or near the excited-state equilibrium geometry, see Fig. 1, effectively quenching the excited-state structural dynamics. When photoexciting at 395 nm the incoming photon has insufficient energy to excite molecules from the bottom of the ground-state potential to the singlet excited-state potential, a process requiring 3.35 eV. However, due to the curvature and relative positions of the potential surfaces, a 395 nm photon does have sufficient energy (3.14 eV) to promote a PtPOP molecule to the singlet excited state potential surface, *if* the Pt nuclei are already in their excited-state equilibrium configuration.

This d_{PtPt}^{gs} -dependence of the $S_0 \rightarrow S_1$ excitation energy is analogous to the R -dependent ionization cross sec-

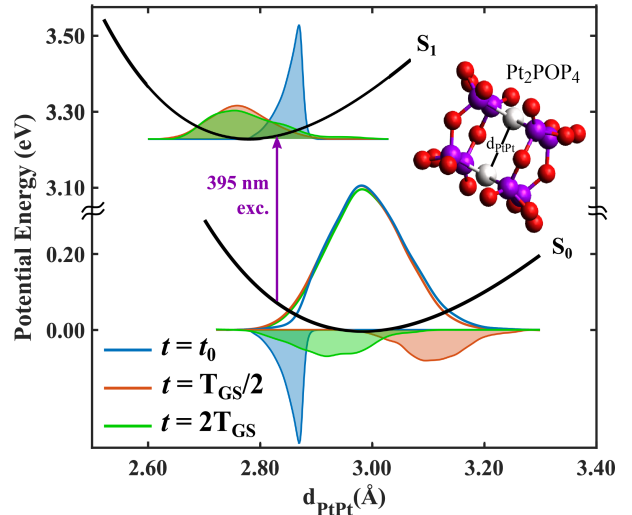


Figure 1. QM/MM simulation of the structural dynamics following photoexcitation at 395 nm. The distribution of Pt-Pt distances in the ground-state ensemble is given by blue/red/green lines, representing the time steps $t = 0$, $t = T_{gs}/2$ and $t = 2T_{gs}$. Shaded areas indicate the corresponding (exaggerated) distribution of the PtPt distances in the S_1 singlet state and the distribution of Pt-Pt distances in the ground-state. An animation of the time evolution can be found in the SI.

tion utilized to create and observe ground-state dynamics in so-called *Lochfrass* experiments [15–19]. The "hole-burning" technique has also been used to investigate ground-state dynamics of e.g. hydrogen bonds in water [38, 39] and Fleming and co-workers [40] have shown that the dynamics of a ground-state non-equilibrium density created by the pump pulse can be modelled through propagation of a so-called hole in the classical ground-state equilibrium distribution mirroring at time zero the distribution promoted to the excited state.

SIMULATIONS

To complement the experimental data and their analysis presented below, the structural hole-burning due to off-resonance excitation of PtPOP was also investigated via hybrid QM/MM BOMD simulations. PtPOP was modelled using density functional theory (DFT) with the BLYP functional [41, 42], and a representation of the Kohn-Sham (KS) orbitals in terms of tzp basis set [43] for the Pt atoms and dzp for the rest of the atoms [43]. The TIP4P force field [44] was used for the surrounding aqueous solvent (cubic box with side length of 35 Å). The simulations were realized using the BOMD code and QM/MM interfacing scheme [32] implemented in ASE [45, 46] and GPAW [47, 48].

To model the off-resonance excitation process, the simulation procedure first established a large set of equi-

brated MD ground-state configurations. From these, a subset with sufficiently short Pt-Pt distances to allow excitation to the first singlet excited-state by a ~ 3.14 eV photon was selected taking into account the spectral width of the excitation pulse. photoexcitation to the S_1 singlet state of PtPOP was modelled by starting 50 independent trajectories from this subset of ground-state configurations using the Δ SCF method [49, 50]. This procedure established two sets of trajectories, representing propagation of a depleted ground-state ensemble and of an excited-state ensemble. Figure 2 shows the d_{PtPt} distributions immediately after the excitation event. The QM/MM BOMD simulation setup is extensively described in the SI, and the results are further discussed below.

We note that the semi-classical picture used to predict the dynamics taking place in the ground state after interaction with a short pump pulse implicitly incorporates effects that are commonly thought of as originating from a combination of absorption and impulsive stimulated Raman scattering [40].

EXPERIMENTAL

Laser-pump/X-ray probe experiments were conducted at the LCLS XFEL facility at SLAC. The XFEL delivered < 50 fs 9.5 keV X-ray pulses at 120 Hz to the XPP experiment station [51], where the X-ray beam was focussed to a $30 \times 30 \mu\text{m}^2$ spot. Laser excitation was by < 50 fs 395(5) nm pulses, focused to a circular spot of $< 50 \mu\text{m}$ diameter and with a pulse energy of $3 \mu\text{J}/\text{pulse}$. The nearly collinear laser and X-ray beams were overlapped spatially and temporally at the sample position. The sample consisted of a $50 \mu\text{m}$ diameter free-flowing cylindrical jet of an 80 mM aqueous solution of PtPOP, with a flow speed sufficient to ensure full sample replenishment between successive pump/probe events (120 Hz). Scattered X-rays were detected by the 2D CSPAD [52] detector positioned ~ 5 cm behind the sample, allowing a Q -space coverage up to $Q = 5 \text{ \AA}^{-1}$, where Q is the magnitude of the scattering vector defined by $Q = \frac{4\pi}{\lambda} \sin(2\theta/2)$ with 2θ the scattering angle. Following detector corrections, background subtraction and outlier rejection as previously described [53], 2D difference scattering images as a function of time were constructed by subtracting laser-off images where the pump laser had not interacted with sample from laser-on images, where the laser had interacted with the sample at time t relative to the X-ray probe. Designating the scattering patterns with and without the excitation laser interacting with the sample as "On" and "Off" the difference signal is defined as

$$\Delta S(t) = S^{\text{On},t} - S^{\text{Off}} \quad (1)$$

For the experiments and analysis described here, the individually calculated difference scattering images were

rebinned and subsequently averaged in 10 fs time bins according to the upstream Timing Tool [54] with approximately 150 images in each bin.

Focusing on the contribution to the scattering patterns from the solute molecules and designating these as either *gs* or *es* corresponding to ground- and excited-state molecules, the "Off" signal is the scattering from just the ground-state equilibrium structure of PtPOP whereas the "On" signal arises from two contributions:

$$\begin{aligned} S^{\text{Off}}(t) &= S^{\text{gs},eq}; \\ S^{\text{On}}(t) &= \alpha S^{\text{es}}(t) + (S^{\text{gs},eq} - \alpha S^{\text{gs},hole}(t)) \end{aligned} \quad (2)$$

-where α denotes the fraction of photoexcited PtPOP molecules in the probed sample volume at the given time delay. The term in the parentheses describes the population of ground state molecules, of which the fraction α has been promoted to the excited state. The difference scattering signal is then given by:

$$\Delta S(t) = \alpha [S^{\text{es}}(t) - S^{\text{gs},hole}(t)] \quad (3)$$

As such, the acquired difference scattering signal arises from both the excited-state population as well as from the "hole" that the excitation pulse created in the ground state.

The 2D difference images as acquired are anisotropic, with the anisotropic contribution to the (difference) scattering arising from preferential excitation of molecules with the transition dipole moment aligned parallel with the polarization of the excitation laser pulse. If the subsequent structural changes have a specific orientation with respect to the transition dipole moment, then the resulting scattering patterns will necessarily be anisotropic. This is the case here, as the $d\sigma^*p\sigma$ absorption peak has a transition dipole moment aligned with the Pt-Pt axis along which the Pt nuclei in the photoexcited molecules contract. The difference scattering signal from such a distribution of solute molecules consisting of N atoms is described by [55–57]

$$\Delta S(Q, t) = \Delta S_0(Q, t) + P_2(\cos(\theta_q)) \Delta S_2(Q, t); \quad (4)$$

Suppressing the time-dependence for clarity of presentation, the isotropic ΔS_0 and anisotropic ΔS_2 signal from the solute can be calculated from:

$$\begin{aligned} S_0(Q) &= \sum_{i,j}^N f_i(Q) f_j(Q) \frac{\sin(Qr_{ij})}{Qr_{ij}}; \\ S_2(Q) &= -c_2 \sum_{i,j}^N f_i(Q) f_j(Q) P_2(\cos(\xi_{ij})) j_2(r_{ij}); \end{aligned} \quad (5)$$

Here, the geometry of the experiment and the solute is introduced through θ_q , the angle between the laser polarization axis and $\mathbf{Q}$, $\mathbf{r}_{ij}$ which is the vector (of length r_{ij}) connecting atoms i and j , and through ξ_{ij} , the angle between $\mathbf{r}_{ij}$ and the transition dipole moment of the

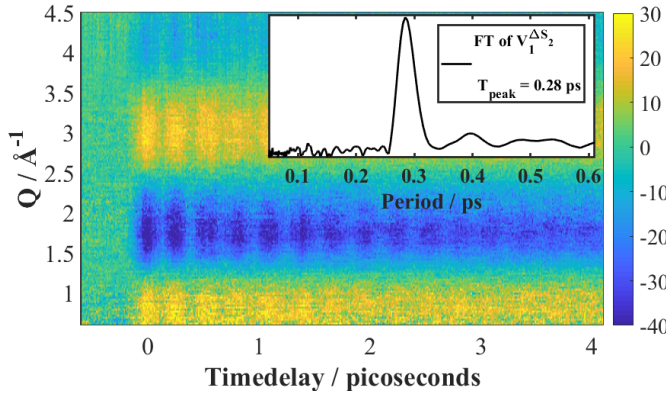


Figure 2. $\Delta S_2(Q, t)$ with the color scale given in %-units of total signal. A pronounced oscillatory pattern is observed, reflecting the change in average Pt-Pt distance in the sample as a function of time. The inset shows the Fourier transform of the first right-singular vector of an SVD analysis, $|\mathcal{F}(V_1^{\Delta S_2})|$. A sharp peak at the $T=0.28$ ps ground-state period of PtPOP is observed.

molecule. P_2 is the 2.-order Legendre polynomial, j_2 the 2.-order spherical Bessel function and f_i refers to the form factor of atom i in the molecule. In a time-resolved experiment all coordinates may depend on t , and the time evolution of the orientational distribution is described by the pre-factor $c_2(t)$ which goes from a maximum value of 2 immediately after the excitation event to a value of 0 after full rotational dephasing [57].

For the structural analysis presented here, the isotropic $\Delta S_0(Q)$ and anisotropic $\Delta S_2(Q)$ contributions to the difference signal were separated as described previously [56, 57]. Below, the analysis is focussed on $\Delta S_2(Q, t)$ with details of the setup, data reduction techniques and partitioning of the scattering signal into $\Delta S_0(Q)$ and $\Delta S_2(Q)$ provided in the SI along with the full analysis of $\Delta S_0(Q, t)$.

Figure 2 shows $\Delta S_2(Q, t)$ with the time delay t along the horizontal axis and Q along the vertical axis. Following photoexcitation at $t = 0$ a positive feature appears at low Q , directly indicative of a decrease in the average Pt-Pt distance in the probed sample volume. In the following picoseconds, the difference signal oscillates in intensity with little change in signal shape. Following a Singular Value Decomposition (shown in the SI) of the data, the insert shows the Fourier transform of the first right-singular vector of the difference signal, $|\mathcal{F}(V_1^{\Delta S_2})|$. From this, we find that structural dynamics of the photoexcited sample gives rise to a difference scattering signal exhibiting a pronounced oscillatory behavior with a period T close to 285 fs (Fig. 2, insert). This value is in very good agreement with the ground-state frequency of the Pt-Pt oscillations as determined by optical and Raman spectroscopy and significantly different from the $T = 210$ -225 fs period of the singlet- and triplet excited

states [22, 27, 29].

These general observations can be directly understood as arising from the structural dynamics following off-resonance excitation: photoexcitation at 395 nm preferentially excites the sub-population of PtPOP molecules with short Pt-Pt distances, that is, near the potential energy minimum of the singlet electronic excited state potential (Fig. 1). The photoexcited molecules thus experience no gradient on the excited state potential, and therefore exhibit little or no coherent vibrational dynamics. Simultaneously, the ground state population as characterized by the distribution of Pt-Pt distances is now no longer in equilibrium as molecules with short Pt-Pt bond lengths have been preferentially excited, creating a "hole" in the electronic ground state population around the $d_{\text{PtPt}} = 2.77$ Å minimum of the excited-state potential surface. As the ensemble of molecules evolves, the ground state population of molecules characterized at $t = 0$ by long Pt-Pt distances ($d_{\text{PtPt}} \sim 3.1$ Å) will after $T^{gs}/2$ have moved to short Pt-Pt distances, thus filling the "hole" at $d_{\text{PtPt}} = 2.77$ Å which consequently moves to longer Pt-Pt distances. Therefore, at $t = T^{gs}/2$ the average Pt-Pt distance in the full ensemble of molecules in the probed sample volume is shorter than before $t = 0$, thus giving rise to the difference scattering signal characteristic of an ensemble having undergone an average Pt-Pt contraction [25, 58]. In the following picoseconds, the hole continues to propagate on the ground state potential surface, eventually broadening to reflect the equilibrium ground-state distribution of Pt-Pt distances.

ANALYSIS AND RESULTS

To quantify the structural dynamics underlying the difference scattering signals shown in Figure 3, the data was analyzed by structural fitting, employing a model incorporating a Pt-Pt distance-dependent depletion of the ground state population. The approach closely follows the analysis presented for the Co(terpy)₂ system by Bisin et al. [4], except that here we focus on $\Delta S_2(Q, t)$ and consider all time evolution to be due to structural dynamics in the ground state rather than in the excited state population.

Within this structural analysis framework [25, 59], the excitation fraction and key structural parameters (here d_{PtPt}) are known to be strongly correlated [60]. To enable the robust determination of bond length dynamics, the excitation fraction was first estimated by analyzing the difference signal at $t = 5$ ps where both the excited and ground state populations can be considered as having reached their equilibrium distributions. The model applied in this step was completely analogous to the one applied in our original synchrotron work on PtPOP [25], consisting of DFT-derived structures for the ground- and excited state of PtPOP while maintaining the excitation

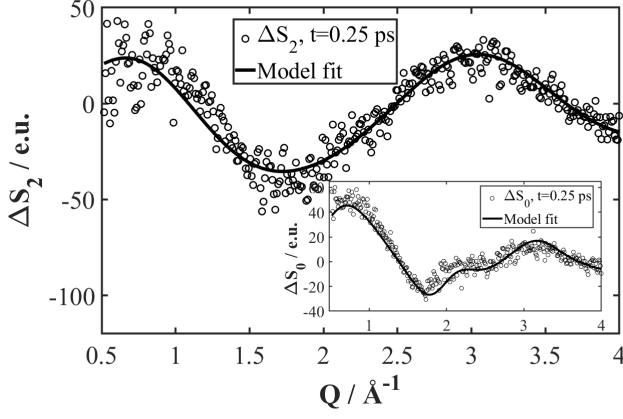


Figure 3. ΔS_2 and model fit at $t = 0.25$ ps after photoexcitation. Insert shows the corresponding fit of ΔS_0 at the same time delay. The fit quality is representative for the full data sets as shown in the SI.

fraction α as a free parameter. Obtaining a photoexcitation fraction $\alpha = 0.018$ through this analysis, the second step of the structural analysis relies on locking this parameter in the analysis of the full data set. The difference signal modeling further assumes the excited state distribution to have $d_{\text{PtPt}} = 2.77$ Å for all time delays, while the ground-state distribution is assumed to be given by a combination of the ground state equilibrium structure minus a (delta-function) hole characterized by a time-dependent Pt-Pt distance $d_{\text{PtPt}}^{\text{hole}}(t)$ as described by Eq. 3. The model with which the observed time-dependent difference scattering signal was fit is thus:

$$\Delta S_2(Q, t) = S_2^{\text{es}}(Q) - S_2^{\text{gs, hole}}(Q, d_{\text{PtPt}}^{\text{hole}}(t)) \quad (6)$$

-with all structural dynamics parameterized through the position of the ground state hole, $d_{\text{PtPt}}^{\text{hole}}(t)$ and with the scattering signals calculated through Eq. 5.

Figure 3 shows the quality of the fit at a representative time delay, $t = 0.25$ ps, and Figure 4A shows the best-fit value for $d_{\text{PtPt}}^{\text{hole}}$ as a function of time delay t . $d_{\text{PtPt}}^{\text{hole}}$ is observed to move towards larger values immediately after excitation and then oscillates around the ground-state equilibrium distance in agreement with the discussion above. The time dependence is very well described by an (IRF-broadened) exponentially damped sine function convoluted with a step function centered at $t = 0$. Fitting this function to $d_{\text{PtPt}}^{\text{hole}}(t)$ we find $T^{\text{hole}} = 0.284(1)$ ps with decay time $\tau^{\text{hole}} = 2.4(2)$ ps. The insert in Figure 4A shows the corresponding results from the analysis of $S_0(Q, t)$ (SI).

As a direct comparison between simulations and experiments, Figure 4B shows the corresponding results of our QM/MM BOMD simulations. From these, we obtain a period of $T_{\text{sim}}^{\text{gs}} = 0.271$ ps, which agrees to within 5% with the experimental data. The decay of the ground-state oscillations takes place in $\tau_{\text{sim}}^{\text{gs}} = 0.7$ picoseconds, somewhat

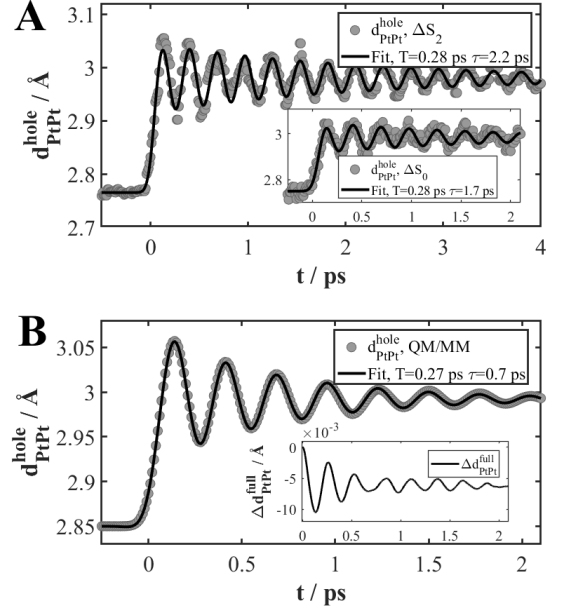


Figure 4. **A**: Time-dependent evolution of the position of the hole in ground-state population of PtPOP (Gray circles) as determined by the structural analysis of the difference scattering signals in Figure 3. The dynamics have been fit (black line) with an IRF-broadened function arising from an exponentially damped sine function convoluted with a step function. Insert shows the corresponding ΔS_0 results. **B**: Time-dependent position of the hole (gray circles) in the QM/MM simulations fitted with the same function (black line) as the experimental results. Insert shows the average Pt-Pt distance for the entire simulated ensemble.

faster than observed. The insert of Figure 4B shows the average Pt-Pt distance for the entire simulated ensemble from which the expected overall decrease in the average Pt-Pt distance is evident.

DISCUSSION

The oscillation period of $T_{\text{hole}}^{\text{gs}} = 0.284$ ps determined by both the fourier transform of the difference signal as well as from the fit of $d_{\text{PtPt}}^{\text{hole}}(t)$ in Figure 4 is in very good agreement with the value reported from optical studies of PtPOP in ethylen glycole where $T^{\text{gs}} = 0.281$ ps was found [27]. The coherence lifetime of $\tau = 2.4(2)$ ps is also in good agreement with previous optical studies of PtPOP and is very close to the $\tau = 2.1$ ps lifetime determined for ground-state dynamics in BF-substituted PtPOP in methanol [29]. We note that even though the decoherence is well captured by a single exponential, the fit at $t < 1$ ps tends to underestimate the observed amplitude of the oscillations in d_{PtPt} . This could indicate either some degree of anharmonicity of the potential surface or a contribution from excited-state dynamics. From the

present data we cannot conclude either mechanism to be dominating, but we note that the third negative peak in $d_{\text{PtPt}}(t)$ shows diminished magnitude in both the S_0 and the S_2 channel in agreement with the QM/MM simulation results (insert of Figure 5B) which has a significantly stronger contribution from excited state dynamics. However, the fourier transform in Figure 2 suggest that the excited state contribution to the observed dynamics is quite small. Further work along these lines will focus on identifying the atomistic mechanism of the decoherence observed and the underlying reason for the significantly faster decay ($\tau = 0.7$ ps) observed in the QM/MM BOMD simulations.

CONCLUSIONS

The experimental data presented here demonstrates the preparation of a vibrationally cold excited-state population and the subsequent evolution of the ground-state hole population. Separating the isotropic S_0 and anisotropic S_2 contributions to difference scattering signal is utilized to obtain a direct view of the structural dynamics of the photoexcited solute molecules, unobscured by the bulk solvent contributions to the difference scattering signal. Analysis of the data relied on simplifying assumptions regarding the population distributions, but direct comparison with QM/MM simulations allowed direct and experimentally supported visualization of how the population distributions evolve on both the ground- and excited state potential surfaces. We expect that future experiments with better Q-space coverage will allow us to follow these dynamics in more detail, as recently discussed from a theoretical point of view [61] and experimentally realized for the $\text{Fe}(\text{bpy})_3$ system using fs-resolved XAFS [8].

A key feature of the present experiment is the controlled preparation of a vibrationally cold excited state through off-resonance excitation. Although beyond the scope of the present study, we suggest that further studies utilizing vibrationally cold excited states may shed light on the temperature-dependent and highly elusive [30] mechanism of the singlet-triplet transition in PtPOP.

In summary, the results presented above demonstrate how excitation with ultrashort optical laser pulses in combination with SASE-based X-ray laser sources can be used to prepare well-defined populations on the ground- and excited-state potential surfaces of molecules in solution and subsequently follow their evolution in detail. In particular, by choosing off-resonance excitation wavelengths, the excited population can be prepared in a vibrationally cold state, allowing accurate tracking of the ground-state dynamics alone. Direct coupling to high-level modeling enables full elucidation of the molecular-level details of the dynamics as they unfold. With the number of XFEL sources rapidly increasing and with the

average brilliance of the sources set to increase by several orders of magnitude, we believe that the methods outlined in this work can have wide-ranging impact on the study of ultrafast structural dynamics in general.

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Paper VIII

Bond formation and structural relaxation in TlPtPOP studied with ultrafast time resolved X-ray scattering.

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Bond formation and structural relaxation of the $\text{TI Pt}_2\text{POP}_4$ complex studied with ultrafast time resolved X-ray scattering

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Abstract goes here...

Introduction

The photochemistry of binuclear $d^8 \cdot d^8$ transition metal complexes has been the subject of intense study over the last couple of decades [source/s]. The interest is in part due to their ability to form photo induced chemical bonds which is not only interesting from a fundamental chemistry bond formation viewpoint but is also of practical interest as the photo induced opening of orbitals may lead to the formation of excited state complexes (exciplexes) with catalytic properties [source/s]. A prime example of an intensively studied $d^8 \cdot d^8$ system is that of the square planar diplatinum complex, tetrakis- μ -pyrophosphitodiplatinate (PtPOP), which has been the subject of optical studies^{1,2} and X-ray studies.³⁻⁶ The significant interest in PtPOP sparked several studies of related complexes in which a metal ion is coordinated to PtPOP .⁷⁻¹⁰ A study by Nagle et al⁷ observed the appearance of two new emission bands with the addition of thallium ions in an aqueous solution of PtPOP . The first emission band to appear with an increase in the concentration of Tl ions was assigned to the formation of the single axially coordinated thallium complex Tl-PtPOP^* while the second emission band was assigned to the doubly axially coordinated $\text{Tl-PtPOP}^*\text{-Tl}$ exciplex. Nagle commented in

an end note that a similar reaction occurred for Ag-PtPOP*. The suggestion of a preassociated metal coordinated complex was further reinforced by Clodfelter.⁸ Clodfelter measured the phosphorescence of Tl and PtPOP in ethylene glycol at 190K where diffusion should be minimal and observed the emission band previously assigned to the Tl-PtPOP* complex by Nagle. This result indicates that thallium is preassociated in the ground state with a conformational structure close to that of the excited state Tl-PtPOP* complex. While the optical studies by Nagle and Clodfelter provides evidence of the ground state complex and exciplex formation of metal coordinated PtPOP. However, no direct structural information can be derived from these optical studies. An issue which can be addressed by either experimental X-ray scattering, X-ray absorption fine structure (XAFS) or from a theoretical Density Functional Theory (DFT) based approach. However, the literature on the structure of metal-PtPOP is limited and conflicting. An X-ray scattering study by Haldrup et al⁹ and a combined X-ray scattering and DFT solution study on excited state Tl and Ag associated PtPOP complexes by Kong et al¹¹ find that the metal ion is axially (end-on) coordinated while a DFT gas phase study of Ag-PtPOP by Kruppa et al¹² suggest that the metal ion is side-on coordinated. The existing X-ray scattering studies of metal coordinated PtPOP⁹⁻¹¹ only deal with the exciplex formation and thus the nature of the preassociated ground state complex, suggested by the work Nagle and Clodfelter, is not well described. Using Time-resolved Wide Angle X-ray Scattering (TRWAXS) this study deals with structural determination of the Thallium preassociated ground state complex, Tl-PtPOP, and the femtosecond structural dynamics of the excited-state Tl-PtPOP* exciplex.

Analysis and results

The TRWAXS data was collected at the XPP end station at the Linac Coherent Light Source (LCLS)¹³ using a standard liquid jet pump probe configuration. The principles of a liquid jet pump probe configuration can be found in the supplementary online of¹⁴ while the

essential experimental parameters are provided in table 1. The 2D X-ray scattering patterns were recorded using the CSPAD detector developed at LCLS.¹⁵ For every 7th X-ray pulse the optical laser pulse was set to arrive after the X-ray pulse yielding X-ray scattering patterns of the unperturbed sample. The data reduction of the patterns follow closely the methods described in¹⁶ and the patterns are corrected for X-ray polarization, detector silicon-absorber-layer efficiency and solid angle coverage. The 2D scattering patterns were azimuthally integrated into 15 slices with each slice having an angle span of 24 degrees. Subsequently the azimuthally integrated curves were corrected for the for X-ray energy arising from the scattering angle being intertwined with the X-ray energy. In addition the curves were corrected for the detectors non-linear intensity response following considerations given in.¹⁷ Using the 15 azimuthally integrated detector slices the isotropic and anisotropic contribution to the signal were separated using the procedure described in.¹⁸ As the isotropic and anisotropic part of the signal both contain the structural information of the sample, the isotropic signal was chosen as for structural analysis as it also contains information of the bulk solvent response. Each difference signal, $\Delta S(Q) = S_{on} - S_{off}$, were created by taking a laser pumped scattering image and subtracting a mean of the 2 nearest neighbouring X-ray patterns where the optical laser pulse had not perturbed the system. The difference signals were time stamped using the XPP timing tool¹³ which allowed the difference signals to be time sorted into equistatistical bins each containing 200 scattering curves resulting a temporal width of ~ 75 fs for each bin.

The difference scattering data was recorded for a sample consisting of a 14 mM PtPOP and 110 mM Thallium trifluoromethanesulfate in an aqueous solution. As reported by Nagle et al⁷ and Clodfelter et al⁸ such a solution will contain a mixture of PtPOP and Tl-PtPOP ground state species. This leads to complex population kinetics upon photo illumination on long time scales (~ 10 -100ps).

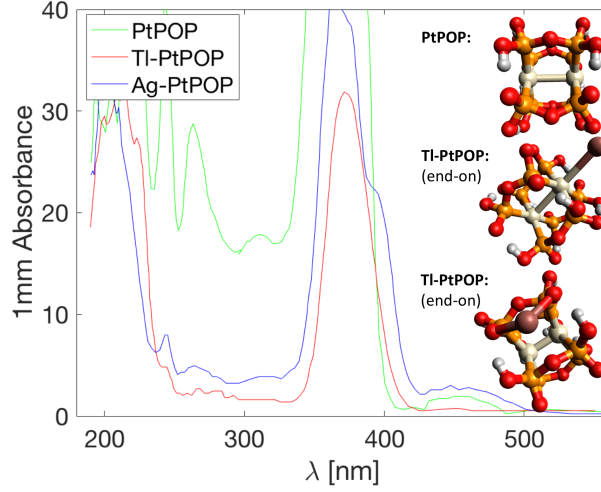


Figure 1: Absorbance measurements on PtPOP and (Tl,Ag)-PtPOP and 3D structures of PtPOP.

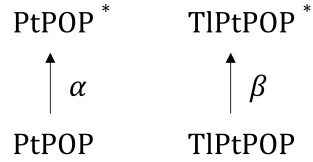


Figure 2: A schematic illustration of the population kinetics. The arrows indicate transition and the labels represents the fraction of the specimen that at any given time is populated ^{1, 8}

At the early sub 10 ps timescale the reaction dynamics is simplified to two reactions products, see figure 2, as additional reaction products only appear for longer time delays where diffusion mechanisms has time to set in. Hence at the sub 10ps timescale we model the system by the sum of the individual dynamics of the solute species, $\text{Tl-PtPOP} \rightarrow \text{Tl-PtPOP}^*$ and $\text{PtPOP} \rightarrow \text{PtPOP}^*$, a solvent contribution as well as solvent-solute cross term. The solvent contribution is a structural change of the bulk solvent as the solvent pair correlation of the solvent changes. This is a consequence of the heating of the solvent as kinetic energy is transferred from the solute to the solvent.¹⁹ The solvent-solute cross term, or cage, is the solvation of the solute as the nearest solvent molecules respond to the structural change of

the solute.²⁰ Thus the time dependent difference scattering is modelled as

$$\begin{aligned} \Delta S(t) = & \alpha(t) \Delta S_{\text{TiPt}_2}(\Delta \bar{\mathbf{R}}_1) + \Delta T(t) \left. \frac{\partial S_{\text{H}_2\text{O}}}{\partial T} \right|_{\rho} \\ & + \beta(t) [\Delta S_{\text{Pt}_2}(\Delta \bar{\mathbf{R}}_2) + \Delta S_{\text{Cage}}], \end{aligned} \quad (1)$$

where the scattering vector Q has been omitted for clarity. Here t is the time delay between the laser pump pulse and the X-ray probe pulse, ΔT is the temperature increase of the bulk solvent, α and β are the fractions of excited TiPtPOP and PtPOP molecules respectively and $\Delta \bar{\mathbf{R}}_x$ refers to the time-dependent changes in geometry of specimen x .

In previous studies of solvated transition metal complexes [REF] it has been shown that the solvent heat response in the first 1-10 ps following excitation is well described by the solvent reference measurement where the solvent response due to heating is measured using a neat solvent and a dye. Thus the model component for the effect of solvent heating is given by the reference measurement found in.²¹

The physics of the PtPOP parent complex

The geometric configurations in PtPOP following excitation at 395nm has been shown to be described predominantly through the movement of the two Pt-atoms due to the rigidity of the ligand [REF: rigid ligand]. Hence the difference signal of PtPOP, $\Delta S(\Delta \bar{\mathbf{R}}_2) = S(\bar{\mathbf{R}}_{\text{Pt}_2}^*(d_{\text{PtPt}}^{ES})) - S(\bar{\mathbf{R}}_{\text{Pt}_2}(d_{\text{PtPt}}^{GS}(t)))$, is a function of the Pt-Pt coordination of the ground state and excited state complex. When photo exciting PtPOP 395 nm the Pt-Pt bond exhibits coherent 285 fs vibrations with a coherence lifetime of $\tau \sim 2$ ps of which the origin is ascribed to wave packet dynamics of the depleted ground state potential energy surface.^{1,2,22} The dynamics of the PtPOP subspecies is modelled as given by the structural dynamics found in.²² The cage term of PtPOP was calculated using QM/MM simulations in a previous study by

¹In this notation it is not directly interchangeable with rate constants, a thorough study of which have been conducted by Clodfelter et al

Determining the ground state structure of TlPtPOP

Assuming the same rigidity of the ligand in Tl-PtPOP as in the parent complex, entails that the ligand structure is also independent on the electronic state of the complex. Thus Tl-PtPOP is similarly parameterized through the two distances of Tl-Pt and Pt-Pt through $\Delta S(\Delta \bar{\mathbf{R}}_1) = S(\bar{\mathbf{R}}_{\text{TlPt}_2}^*(d_{\text{PtPt}}^{ES}(t), d_{\text{TlPt}}^{ES}(t))) - S(\bar{\mathbf{R}}_{\text{TlPt}_2}(d_{\text{PtPt}}^{GS}, d_{\text{TlPt}}^{GS}))$. In previous studies of the structural dynamics of TRWAXS data the structural dynamics of the solute is found from the structural parameterization of the excited state structure while the ground state structure is known and thus locked to the known geometry.^{14,23} However, for the case of TlPtPOP the situation is reversed as the ground state structure is unknown while the vibrationally relaxed excited state structure is known from a combined X-ray scattering and DFT study of the excited state complex formation, $\text{PtPOP} + \text{Tl} \rightarrow \text{TlPtPOP}^*$.^{9,11} The ground state structure is found from structural optimization through model fitting of the experimental difference signal averaged from the delays $t \in [4, 5]$ ps. At $t \in [4, 5]$ ps TlPtPOP exist in a vibrationally cold excited state which enables the ground state structure to be optimized by fixating the geometry of the excited state structure to the structure reported by.¹¹

Coordination site of the metal ion

Two possible coordination sites for metal ion and PtPOP have been suggested: **1)** a side-on coordinated structure, $\bar{R}_{side}$, suggested from gas-phase DFT of Ag-PtPOP by Kruppa et al¹² where the metal ion associate perpendicular to the Pt-Pt bond Kruppa et al suggest that the Pt-Pt bond dynamics is virtually unaffected by the presence of the side-on coordinated ion, effectively reducing the modelling of $\Delta \bar{R}_{side}$ to be parameterized through only $d_{\text{Pt-Pt}} \rightarrow d_{\text{Pt-Pt}}^*$ and a specific location of the metal/Tl atom. **2)** an end-on coordinated structure, $\bar{R}_{end}$, where the Tl atom coordinates along the Pt-Pt axis as suggested by Kong et al¹¹ based on XDS and

DFT studies conducted on the solvated complex. In this model we explicitly assume that the excited state structure found by Kong is correct. This geometry was modelled through the two parameters $d_{\text{Pt-Pt}} \rightarrow d_{\text{Pt-Pt}}^*$ and $d_{\text{Tl-Pt}} \rightarrow d_{\text{Tl-Pt}}^*$, taking $d_{\text{Pt-Pt}}^*$ and $d_{\text{Tl-Pt}}^*$ from the suggested DFT geometry. Both models were tested against the difference signal averaged at $t \in 4\text{-}5$ ps and compared in a χ^2 framework, $\chi^2 = \frac{1}{N-M-1} \sum_Q \frac{[\Delta S_{\text{Model}}(Q) - \Delta S_{\text{Data}}(Q)]^2}{\sigma_Q^2}$, where N is the number of independent data points, M is the number of free parameters and σ is the data related noise. As an estimate of σ , the amplitude of the noise is found by local polynomial fitting as in.⁴ The model parameters of α , β and ΔT were set as free parameters while the geometric parameterization of both the $\bar{\mathbf{R}}_{\text{side}}$ and $\bar{\mathbf{R}}_{\text{end}}$ was implemented through a linearly spaced grid of possible Pt-Pt and Pt-Tl distances. The best fit models of the side-on and end-on coordinated ground state is shown against the time averaged data in Figure 3.

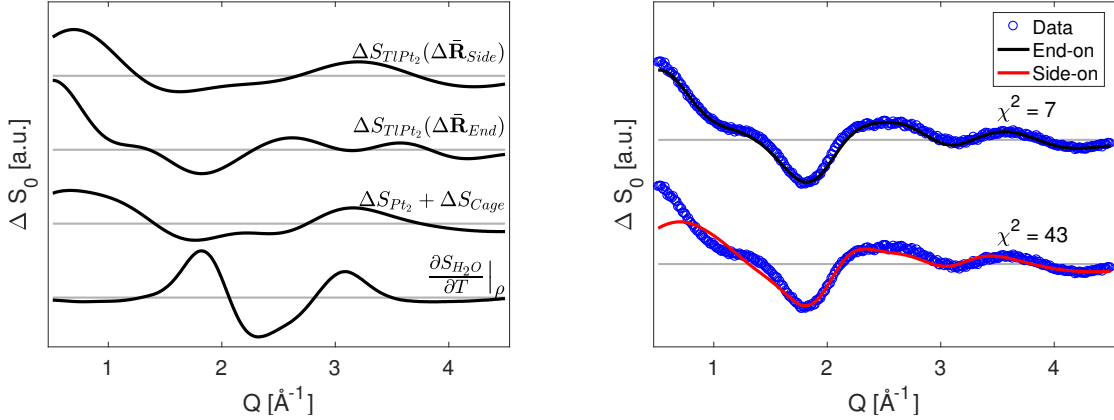


Figure 3: A comparison of the end-on and side-on coordinated models fitted to the $\Delta S(Q)$ averaged from $t \in [4, 5]$ ps. The two model fits are offset for clarity.

For the model of end-on coordinated Tl we find a χ^2 minimum value of 7 while for the side-on coordinated Tl we find a χ^2 minimum of 43. The comparatively large χ^2 values for the side-on coordinated model demonstrates the models inability to describe the data and is thus rejected as a viable structural candidate. For the end-on ground state model we find a χ^2 minimized ground state structure with $d_{\text{Pt-Pt}} = 2.94 \text{ \AA} \pm 0.32$ and $d_{\text{Pt-Tl}} = 3.44 \text{ \AA} \pm 0.28$. The uncertainty estimates are found from the projection of the multidimensional

$\Delta\chi^2$ contours onto the $\Delta\text{Ti-Pt}$ and $\Delta\text{Pt-Pt}$ plane as shown in Figure 4.

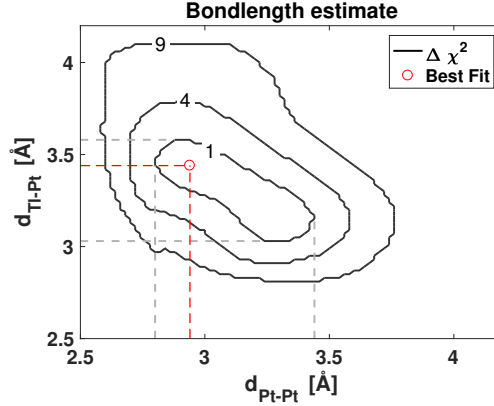


Figure 4: The iso-contours of the $\Delta\chi^2$ surface shown in a coordinate system spanned by the ΔPtPt and ΔTiPt structural parameters. The grey lines indicate the projection of the confidence intervals, and the red indicate the best fit value.

The $\Delta\chi^2$ iso-contours of $\Delta\chi^2 = 1, 4, 9$ corresponds to $1\sigma, 2\sigma$, and 3σ .^{25,26}

The excited state dynamics of TlPtPOP

Using the optimized ground state structure the structural dynamics of TlPtPOP is uncovered by structural optimization of the excited state DFT structure each $\Delta S(t)$. In the excited state structural optimization the Pt-Pt and Pt-Tl bond lengths is set to vary freely. From the analysis of the 5 ps ΔS we find the excitation fractions $\alpha = 4.81 \pm 0.03 \%$ and $\beta = 5.38 \pm 0.10\%$. Ideally the excitation fractions should appear instantaneous with regards to the XFEL time resolution but are smeared due to the instrument response function (IRF) of the experiment. Thus the temporal behaviour of α and β are in reality, $\alpha(t) = \alpha \cdot \text{IRF}(t)$, $\beta(t) = \beta \cdot \text{IRF}(t)$. The IRF can be modelled as the convolution of a Gaussian shaped pulse and a step function resulting in, $\text{IRF}(t) = 1/2(\text{erf}((t - t_0)/\Delta t) + 1)$, where erf is the error function and Δt is the width of the Gaussian shaped pulse, estimated to a value of ~ 75 fs. The number of free parameters of the TlPtPOP model is three, the Pt-Pt and Ti-Pt bond length and ΔT . Figure 5 shows the evolution of the excited state Ti-Pt and Pt-Pt bond lengths of the Tl-PtPOP* exciplex obtained from fitting.

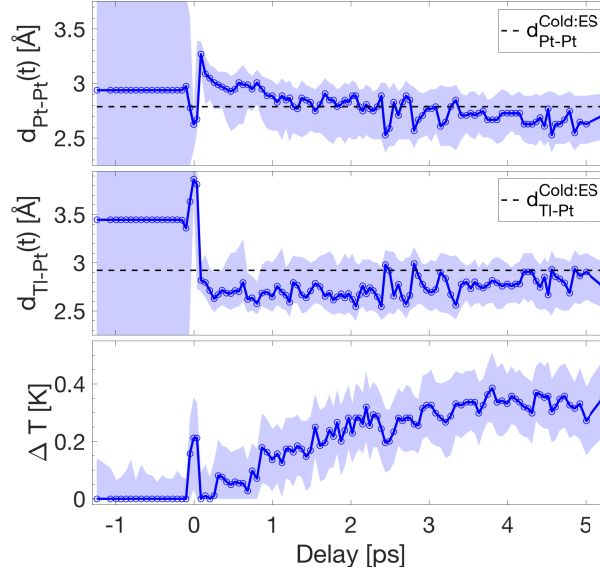


Figure 5: The time dependent evolution of the Pt-Pt bond (top), Pt-Tl bond (middle), and temperature increase of the bulk solvent (bottom) following photo excitation of TlPtPOP at 395 nm. The 1σ confidence intervals are shown as the colored shade. Due to the temporal evolution of $\alpha(t < 0) \sim 0$ the uncertainties of the structural parameters are naturally huge. Notice in particular the immediate contraction of the Tl-Pt bond length in contrast to the Pt-Pt bond length.

We find an immediate contraction of the Tl-Pt bond length followed by a slower contraction of the Pt-Pt bond length reaching a Pt-Pt equilibrium distance after a few picoseconds.

Table 1: Caption

X-ray pump Energy	9.5 keV (0.2% bandwidth)
X-ray pulse temporal width	30 fs (fwhm)
X-ray focal spot size	$\sim 100 \mu\text{m}^2$
Laser pump wavelength	$395 \text{ nm} \pm 5 \text{ nm}$ (fwhm)
Laser pulse temporal width	80 fs (fwhm)
Laser pulse energy per pulse	5 μJ
Laser focal spot size	$\sim 100 \mu\text{m}^2$
Liquid jet (circular) diameter	100 μm
Liquid jet flow velocity	$\sim 1.5 \text{ m/s}$
PtPOP concentration	12 mM
$\text{CF}_3\text{O}_3\text{STl}$ concentration	110mM
Sample-to-detector distance	$\sim 5.1 \text{ cm}$

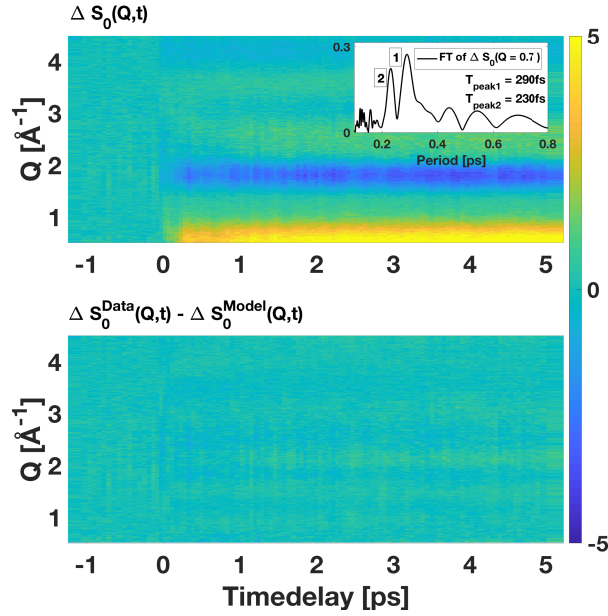


Figure 6: Measured difference scattering signal $\Delta S(Q, t)$ (top) and the residual after best fit model subtraction (bottom). The color scale is given in e.u./molecule $\cdot 10^{-2}$. The inset top right hand side shows a Fourier transform of the time-resolved difference scattering intensity profile which is found from the $\Delta S(t)$ Q-averaged at $Q \in [0.5, 0.7] \text{\AA}^{-1}$

Discussion

Conclusion

Acknowledgements

DANSCAT (I GUESS?) Etc.

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Paper IX

Improving structural determination with high energy TR-WAXS.

Mads G. Laursen, Asbjørn Molkte, Elisa Biasin, Kristoffer Haldrup, Frederik Beyer, Kasper Skov Kjær, Tim Brandt van Driel, Tobias Harlang, Martin M. Nielsen.

Improving structural determination with high energy TR-WAXS

Abstract

Common for the European XFEL, SwissFEL and LCLS-II is that each facility promise access to unprecedented high energy X-rays with high peak brilliance. In this paper we examine the importance of an increase in X-ray energy for the structural analysis of Time Resolved Wide Angle X-ray Scattering difference signals. We show *"insert sentence here"*

Introduction

In the last two decades Time Resolved Wide Angle X-ray Scattering (TR-WAXS) has become a well established technique at synchrotrons and X-ray Free Electron Lasers (XFEL's). In a TR-WAXS experiment the photochemical response of a molecular system in solution is first initiated using an optical laser pump. Subsequently, an X-ray pulse probes the molecular system. The X-ray pulse is scattered of the molecular system and the scattered radiation is collected by a detector. The X-ray scattered intensity contains information about the molecular structure and thus by varying the time of arrival between the laser pump and X-ray probe the structural dynamics of the molecular system can be investigated. TR-WAXS, often in combination with X-ray spectroscopies, has been successful in uncovering the physics of photo-active systems ranging from small transition metal complexes [1–4] to large proteins [5, 6]. The amount of structural information that can be obtained from a TR-WAXS study is discussed in [7] and is related the number of independent data points of a TR-WAXS signal. The number of independent data points, N is expressed as $N = 2\Delta Q D_{max}/\pi$ where ΔQ is the range of scattering vectors (momentum transfers), of the scattered photons [15] and D_{max} is the size of the molecular system. In [7] it is suggested that the access to higher X-ray energies (and thus larger scattering vectors) allows for finer structural determination of TR-WAXS data. Synchrotrons as opposed to XFEL's provides high energy X-rays but lack the time resolution and the peak brilliance of an XFEL. Access to high energy X-rays in combination with femtosecond time resolution and high peak brilliance is promised with the commissioning of the European X-ray Free Electron Laser. For the Swiss Free Electron Laser and the upgrade of Linac Coherent Light Source (LCLS-II), higher X-ray energies can be reached with higher harmonics though at the price of a reduced X-ray brilliance. Thus

with the imminent new XFEL facilities, it is possible to design future high energy TR-WAXS experiments potentially revealing new chemical insight on the femtosecond timescale.

This paper is structured as follows: In section **PtPOP** we introduce the PtPOP system. In section **Method** we describe the procedure with which the TR-WAXS experiments was simulated. In **Quantitative interpretation of the simulated data** we describe the structural analysis framework.

TR-WAXS difference signals

In a TR-WAXS experiment the scattered intensity, $S(Q)$, at a given scattering vector, $Q = 4\pi/\lambda \sin(2\theta/2)$, is determined by the X-ray energy and the probed molecular structure and is given by

$$S(Q) = r_0^2 \sum_{i,j}^N f_i^* f_j e^{i\mathbf{Q} \cdot \mathbf{r}_{ij}}, \quad (1)$$

where $f_{i,j}$ is the atomic form factor, and r_{ij} is the atomic distance between the i 'th and the j 'th atom. A central part of a TR-WAXS is to connect the photochemistry with the structural dynamics of a system. This can be accomplished through the structural analysis of the experimentally obtained difference signals. These difference signals are created by subtracting the X-ray scattering, $S(Q)$, of the unpumped molecular system from the laser pumped molecular system. The X-ray scattering images of the laser unpumped/pumped system is referred to as off/on respectively and thus the difference signal may be expressed as

$$\Delta S(Q) = S(Q)_{on} - S(Q)_{off}. \quad (2)$$

As seen by Equation 1 the X-ray scattering signals of $S(Q)_{on}$ and $S(Q)_{off}$ both contain information on molecular structures of the solute and solvent molecules. However, the scattering signals consist of a static and a dynamical contribution arising from the ground state and the excited state molecules. The ratio of the static and dynamical contribution is typically on the order of 1:100 and the static contribution is removed when investigating the difference signals. With the removal of the static background what remains is the information about the structural changes occurring in the solute and solvent as a result of the laser-induced change of electronic orbitals of the solute. In the ideal experiment the laser pump pulse excites the solute which as a result may undergo a structural change due to laser-induced bond breaking, bond formation, bond contraction/elongation of existing bonds, spin change or a combination of these. In turn a structural change or vibrational excitation of the solute may lead to the rearrangement of the solvent molecules in proximity of the solute. The interplay of the nearest solvent molecules is referred to as the solvent cage or solvent-solute interaction. Over time the excited structure may transfer kinetic energy to the solvent changing the radial distribution function of the bulk solvent resulting in a temperature increase or a density change.

Structural analysis of difference signals

In a TR-WAXS structural analysis, the experimental difference signals are compared to a set of structural models. Several approaches to determine the most likely model exist. In this paper we compare models in a reduced χ^2 framework with

$$\chi^2 = \sum_Q \frac{[\Delta S_{Model}(Q) - \Delta S_{Data}(Q)]^2}{\sigma_Q^2} / (N - M - 1), \quad (3)$$

where $\Delta S_{Model}(Q)$ is the difference scattering from the structural model, $\Delta S_{Data}(Q)$ is the experimental data, N is the number of data points, M is the number of free parameters and σ is the data related noise. Because of the multiple structural changes that can occur in the solute and solvent a structural model is commonly subdivided into the structural difference signal contributions arising from the solute, the solvent and the solvent-solute cage i.e

$$\Delta S(Q)_{Model} = \Delta S_{Solute} + \Delta S_{Solvent} + \Delta S_{Cage}. \quad [22] \quad (4)$$

Simulating ground and excited state 2D scattering patterns

In order to keep as close a connection to experimental conditions as possible the 1d $S(Q)$ curves is simulated using the following scheme. The starting point is to simulate the 2D scattering patterns as would be recorded in a TR-WAXS experiment. To simulate 2D scattering patterns with a pixel resolution of 1-2 million pixels as would be the case of the CSPAD [23], the LPD [25] or the Pilatus detector [24] is unnecessary as the azimuthal integration of the 2D scattering patterns does not require a 1-2 million pixel resolution. This is because the orientational averaged scattering is a slow varying function in Q -space. The scattering patterns are instead simulated 500x500 pixel detector with each pixel covering an area of 440x440 μm . The sample-to-detector distance is chosen as 5 cm allowing for scattering angles up to ≈ 71 degrees to be simulated. The probed sample volume is set by a liquid sheet thickness of 300 μm combined with an X-ray cross section of 100x100 μm . The simulated sample volume contains a 12 mM concentration of PtPOP in neat water and is probed by 10^{12} photons per pattern simulated. The 10^{12} photons per scattering pattern approximately corresponds to the number of photons contained within an X-ray pulse at LCLS. The total scattering simulated for the detector is the coherent and incoherent sum of the X-ray scattering of the sample,

$$S = S_{Coherent\ Solute} + S_{Incoherent\ Solute} + S_{Coherent\ Solvent} + S_{Incoherent\ Solvent}. \quad (5)$$

The incoherent scattering of the solvent is calculated while for the coherent scattering of the solvent a reference is used [19]. The energy dependant fluorescence contain no structural information but contributes to the counting noise. For the sake of simplicity it is omitted.

The combination of sample/detector geometry, sample concentration, # photons, molecular form factor and scattering cross section determines the intensity seen by the detector. In turn the intensity determines the associated Poisson noise seen by each pixel in the corresponding detector scattering pattern. The underlying readout noise of each pixel is set to 10^4 photons/pixel which is one order of magnitude higher than the readout noise of

CSPAD in the high gain mode. However, the simulated detector has roughly 1 order of magnitude fewer pixels and thus the readout noise is comparable to that of the CSPAD when operating in the high gain mode. The readout noise is modelled as Poisson distributed and is centred around zero counts. Centering the noise around zero corresponds having performed a subtraction of the signal contribution arising from the dark current response of the detector. The simulated detector pattern is corrected for solid angle [21], X-ray polarisation [19] and detector absorption layer efficiency [20]. The detector absorption efficiency is calculated for each pixel having a silicon absorber layer with a thickness of $500 \mu\text{m}$. The relative magnitude of the three corrections are shown in Figure 1.

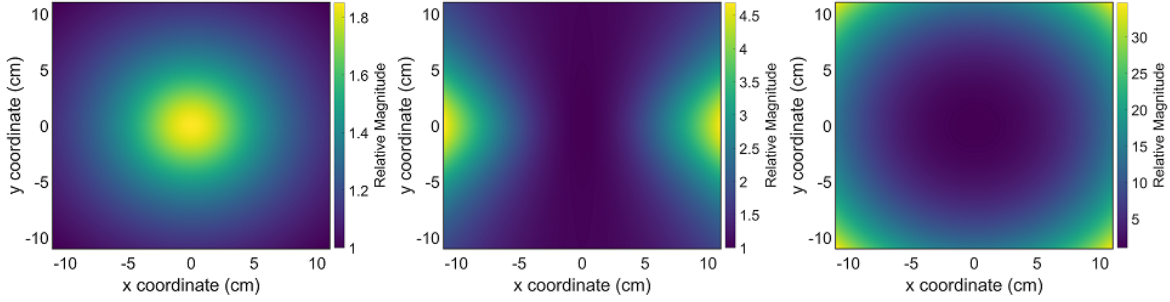


Figure 1. The detector corrections applied in the simulation of scattering patterns. Displayed as the relative magnitude for the chosen detector geometry. Left: Detector absorption efficiency. Middle: X-ray polarisation. Right: Solid angle coverage.

The left hand side of Figure 2 shows the theoretical 2D scattering of the ground state and on the right-hand side the corresponding 1d scattering contributions are displayed.

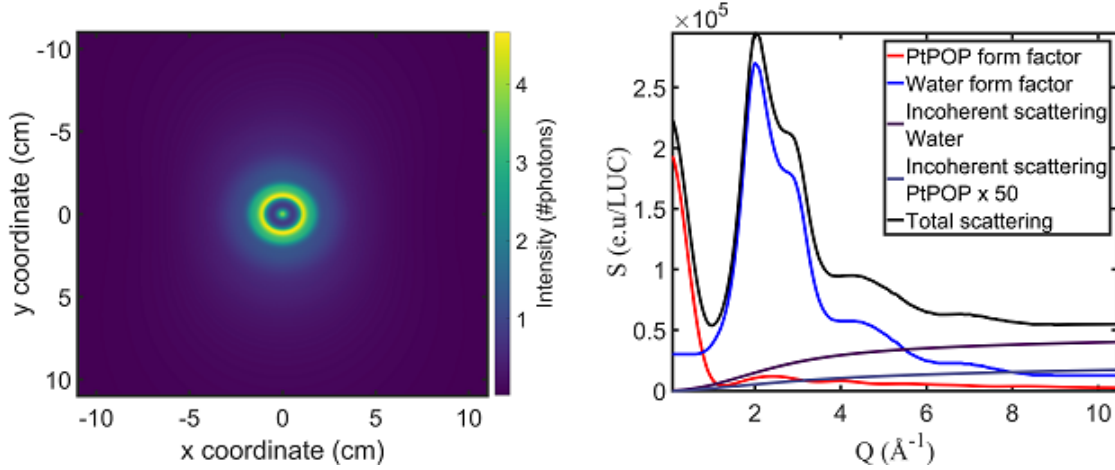


Figure 2. Left: Theoretical scattering pattern shown without the applied detector corrections. The colorbar shows the scattering intensity (if multiplied by 1000. I will add a 10^4 later). Right: the azimuthally integrated contributions of the 2D scattering pattern. Shown for a liquid unit cell.

The 2D scattering pattern of the ground state is subtracted from the 2D scattering pattern of the excited state and subsequently azimuthally integrated giving the 1D difference scattering

signal, $\Delta S(Q)$. The $\Delta S(Q)$ are simulated for a Δ PtPt of 0.2 Å corresponding to DFT simulations of the ground state and the triplet excited state of PtPOP. Furthermore the α and the ΔT is chosen as 20 % and 0.4 K respectively and have magnitudes commonly found in TR-WAXS studies. The left-hand side of Figure 4 shows the three signal contributions of the difference signal which when combined constitute the simulated difference signal as shown on the right-hand side of the figure for 6, 12 and 18 keV.

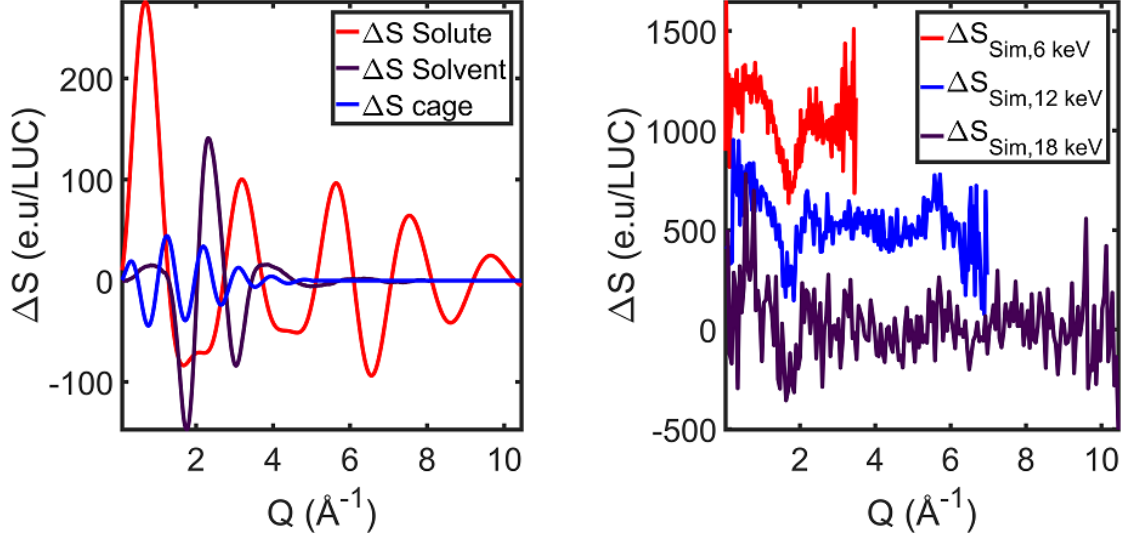


Figure 3. Left: The azimuthally integrated theoretical $\Delta S(Q)$ scattering curves. Right: Azimuthally integrated simulated $\Delta S(Q)$ scattering curves. Shown for 6, 12 and 18 keV.

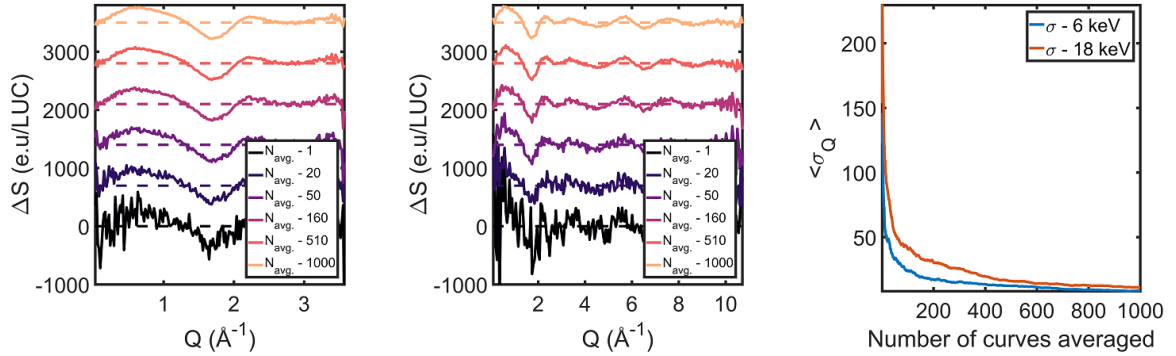


Figure 4. Left and Middle: Azimuthally integrated simulated $\Delta S(Q)$ scattering curves shown for the average of multiple $\Delta S(Q)$. Simulated for 6 and 18 keV. Right: The average of the noise associated to the $\Delta S(Q)$ curves of 6 and 18 keV.

The $\Delta S(Q)$ signals are calculated for X-ray energies from 6-18 keV in steps of 0.5 keV. For each X-ray energy a 1000 2D scattering patterns are simulated for the ground state and the excited state. From these the resultant 1000 2D difference patterns are azimuthally integrated giving for each energy a total of 1000 1D $\Delta S(Q)$. Left-hand side and middle of Figure 4 shows the averaged $\Delta S(Q)$ curves for 6 and 18 keV respectively. On the right-hand

side of Figure 4 the progression of corresponding mean noise, $\langle\sigma(Q)\rangle$, of the $\Delta S(Q)$ of 6 keV and 18 keV is shown for the progressively averaged ΔS scattering curves.

Quantitative interpretation of the simulated data

Each 1D difference signal is compared to two groups of complete and incomplete base models. The purpose of comparing a complete and an incomplete model is to investigate if the additional Q-space coverage, acquired for larger E_{max}^{X-ray} , provides sufficient additional information for the better determination of the simulated parameters despite the model being incomplete. The incomplete model miss the structural contribution from the solvent cage and is only modelled as the combined difference scattering of the solute and the solvent. The missing cage contribution for the incomplete model is primarily dominant in the low Q region ($Q \in [0;5]$). Thus as the Q-space coverage increases the missing cage contribution is weighted less compared to the weight of the solute contribution which is significant for the entire Q-space range. The complete model is complete in the sense that the three structural contributions with which the TR-WAXS data is simulated is used in the complete model. A complete models ability to correctly describe data should be independent of the X-ray energy and thus the complete model serves as a reference frame. The complete model, ΔS_{CM} , consists of a parametrization of the tree structural terms of which the difference signals are simulated. The solute term represents the structural changes of the solute. For the specific case of PtPOP the primary structural change is the PtPt distance. The solvent term arises from the change in the pair correlation function of the solvent due to heating. The solvent-solute cross (or cage) term represents the solvent molecules in proximity of the solute structurally differ from the bulk solvent due to solute-induced solvent rearrangement. The complete model, ΔS_{CM} , is expressed as:

$$\Delta S_{CM} = \alpha \cdot (\Delta S_{sol}(PtPt) + \Delta S_{cage}) + \Delta T \cdot \Delta S_{\Delta T}, \quad (6)$$

while for the incomplete model ΔS_{INCM} the cage term is omitted,

$$\Delta S_{INCM} = \alpha \cdot \Delta S_{sol}(PtPt) + \Delta T \cdot \Delta S_{\Delta T}. \quad (7)$$

In Equations (6) and (7) α is the excited state fraction of the solute and ΔT is the temperature increase of the solvent. The $PtPt$ of the solute term refers to the parametrization of the PtPt distance of the excited state of the solute. The excited state fraction, α , the temperature increase, ΔT and the $PtPt$ distance of the solute are free parameters within the limits of a predefined grid-based parameter space. The grid has the dimensions 91x161x500 and confines α in the range of 0-100%, ΔT in the range 0-0.8 K and the PtPt distance of the excited state in the range 1.768 - 3.768 Å. Each point of the grid thus gives rise to a unique model. For each model a χ^2 value is assigned when compared to a $\Delta S(Q)$. The resultant 3D χ^2 solution space is subsequently converted to likelihood space through the relation,

$$L(P1, ..., P_m) \propto e^{\frac{-\chi^2}{2}}, \quad (8)$$

where L is the likelihood for the parameter set of $P1, ..., P_m$. The 1,2,3- σ are the confidence intervals corresponding to 68.28%, 95.45% and 99,73% [17, 18]. The hypersurfaces defined by 1,2,3- σ contours of the 3D maximum likelihood space is projected onto the parametrization-surfaces which gives the 2D likelihood maps. These hypersurfaces have three projections.

These three projections represent: The correlation between the PtPt distance and the excitation fraction, shown in Figure 5, left; The correlation between PtPt distance and the temperature increase, shown in Figure 5, middle and the correlation between the excitation fraction and the temperature increase, shown in Figure 5, right. Similarly the 2D likelihood correlation maps are projected onto their respective parameter axes and from these the full width of the projection is the uncertainty of the maximum likelihood value of a given parameter. The consequence of correlated parameters is that each parameter is poorly determined. Strong correlations are thus problematic as it may lead to two widely different structural solutions being equally likely.

Correlation between parameters

The challenge of simultaneous determination of a set of parameters is encoded in the parameters correlation factor. The correlation factor may be extracted from the 2D correlation maps by computing the Pearson linear correlation factor,

$$r = \frac{\sum_i (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_i (x_i - \bar{x})^2} \sqrt{\sum_i (y_i - \bar{y})^2}} \quad [18], \quad (9)$$

where (x_i, y_i) are the pairs of points contained within 1σ contour of a given 2D correlation map. Figure 5 shows the three 2D correlation maps associated with the maximum likelihood analysis of the $\Delta S(Q)$ simulated for 9 keV.

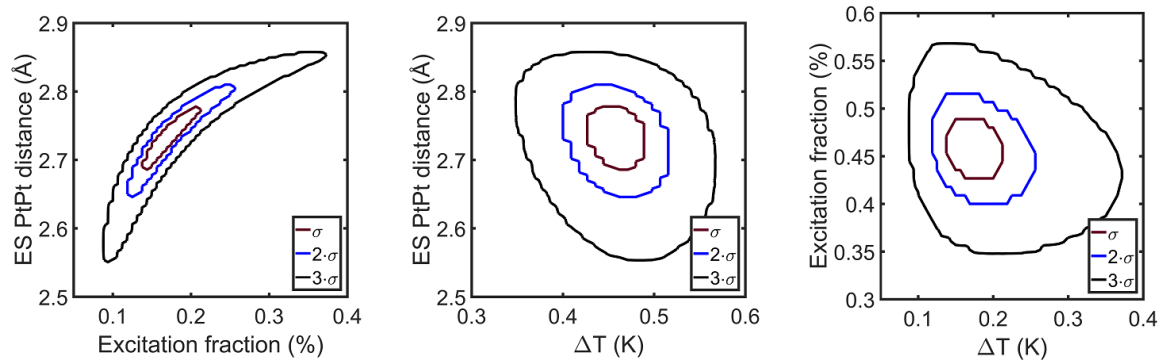


Figure 5. The correlation maps found from the maximum likelihood analysis of the $\Delta S(Q)$ simulated for 9 keV. Left: Excited state PtPt distance vs the excitation fraction. Middle: Excited state PtPt distance vs the temperature increase. Right: The excitation fraction vs the temperature increase

The r , as calculated for the pairs of points contained within 1σ of the three 2D correlation maps is 0.8544, -0.1041 and -0.0462 respectively. Values of r close to zero indicate that the correlation is small while values close to 1 or -1 represents strong correlation or anti-correlation. A significant correlation primarily exist between the excited state PtPt distance and the excitation fraction. Figure 6 shows the r values for the three correlation parameters as a function of the X-ray energy.

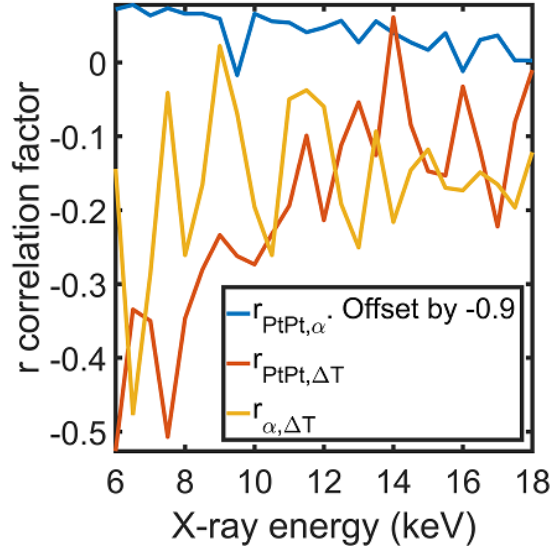


Figure 6. The Pearson correlation factor shown for the three correlation maps as a function of X-ray energy.

From the figure it is seen that the strength of the correlations decrease. However, a significant correlation between the PtPt distance and α remain significant.

Best fit model parameters

In addition to the r value of the 2D correlation maps, other key values which can be extracted from the correlation maps are the minimum χ^2 and the associated best fit parameter values. Figure 7 shows the $\Delta S(Q)$ and the best fit model for the X-ray energies of 6, 12 and 18 keV. The right hand side of the figure shows the χ^2 value of the best fit as given for the complete and incomplete model for the entire X-ray energy range.

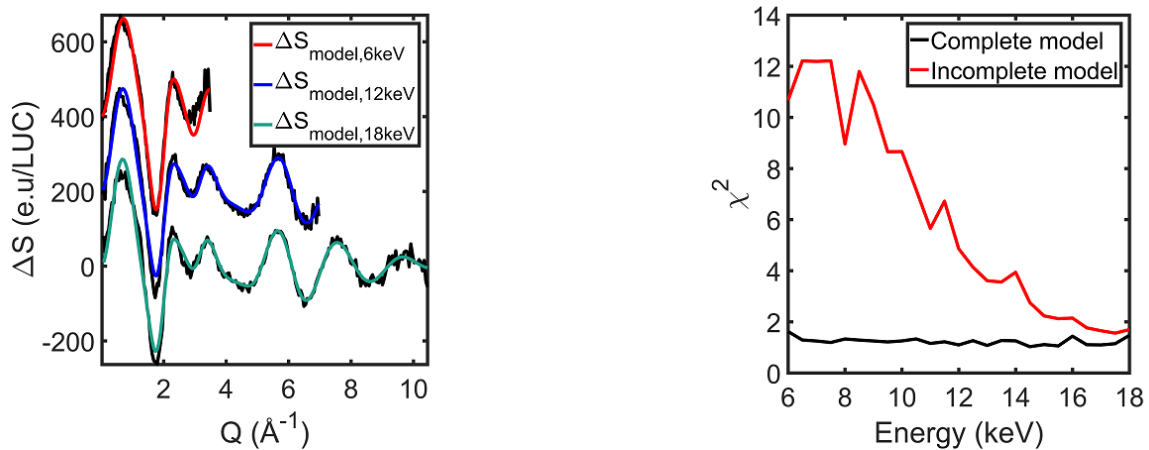


Figure 7. Left: The simulated difference signals averaged for a 1000 shots and the best fit results for 6, 12 and 18 keV. Right: Energy evolution of the minimum χ^2 .

As the Q-space coverage is extended the χ^2 values of the best fit model improves for the incomplete model while the χ^2 of the complete model is largely unaffected. The energy evolution of the best fit parametric values of the complete and incomplete model are shown in Figure 8.

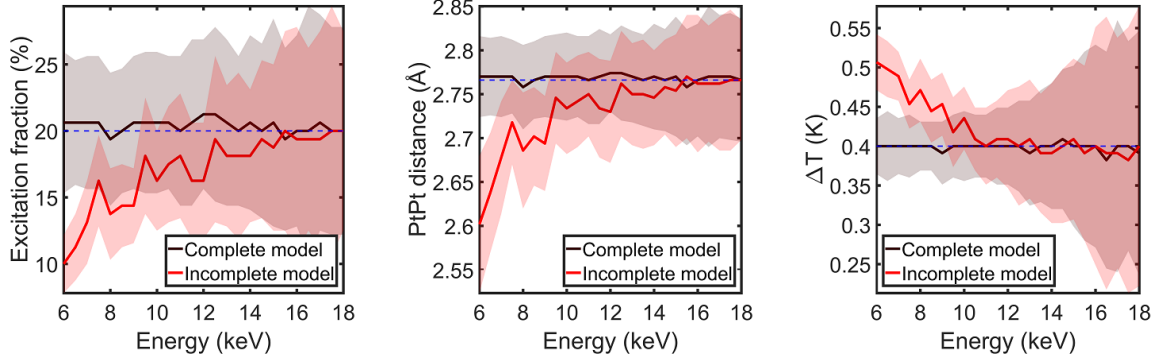


Figure 8. Energy evolution of the parametric values associated with the minimum χ^2 fit. The shaded area of the plot is the 1σ uncertainty of the related parameter. The blue dashed line indicates the parameter value with which the $\Delta S(Q)$ is simulated. Left: Excitation fraction Left: ES PtPt distance. Right: ΔT .

Two things are immediately evident. First, the incomplete models ability to correctly predict the parameter values of the simulation is improved as the X-ray energy increases. Secondly, the increase in parameter precision comes at the price of a decrease in the certainty. This is related to the noise of each Q-bin which changes as the X-ray energy changes. As the X-ray energy increases the noise of the low Q region also increases. This is because the majority of the pixels of the detector is moved towards larger Q-scattering vectors as the X-ray energy increases. The pixel count for each Q scattering vector is shown in Figure 9 for multiple X-ray energies.

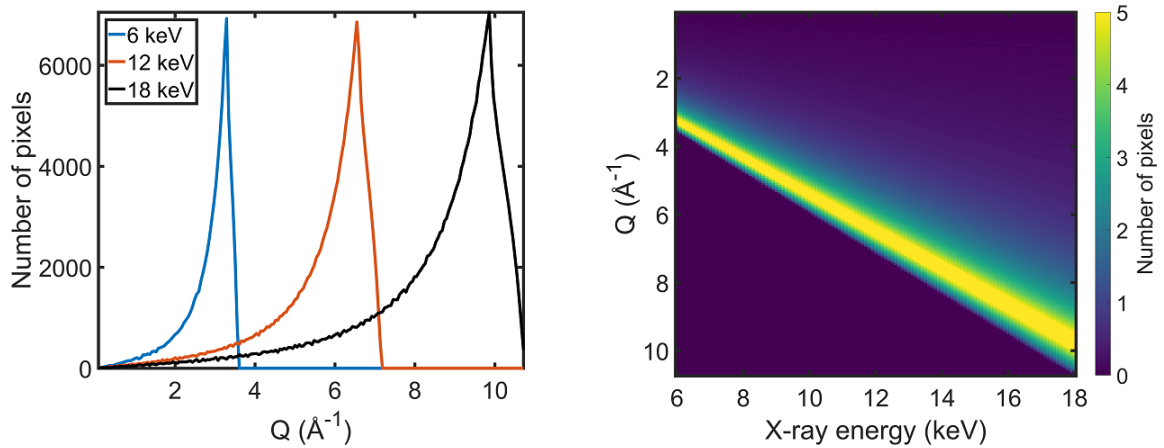


Figure 9. The number of pixels found for each Q scattering vector shown for different X-ray energies. Left: Pixel per Q profile shown for 6, 12 and 18 keV. Right: Pixel profile per Q shown as a colormap for energies between 6 and 18 keV. (colorbar needs to be multiplied by 1000)

As the solute contribution is dominant for the entire Q -range the uncertainty of this parameter does not suffer to the same extend as uncertainty of the α and ΔT parameters.

The effect of noise in model determination

The effect of the noise for the model determination was examined by comparing the structural analysis of the $\Delta S(Q)$ signals which are averaged over a different number of curves. Figure 4 shows the progressively less noisy simulated difference signals. The incomplete model was fitted to each of the noisy simulated difference signal, $\Delta S(Q, \#shot.avg, E)$, with the same procedure described in the Method section. The best fit parameters, now a function of both the number of shots averaged and the X-ray energy, are shown in Figure 10

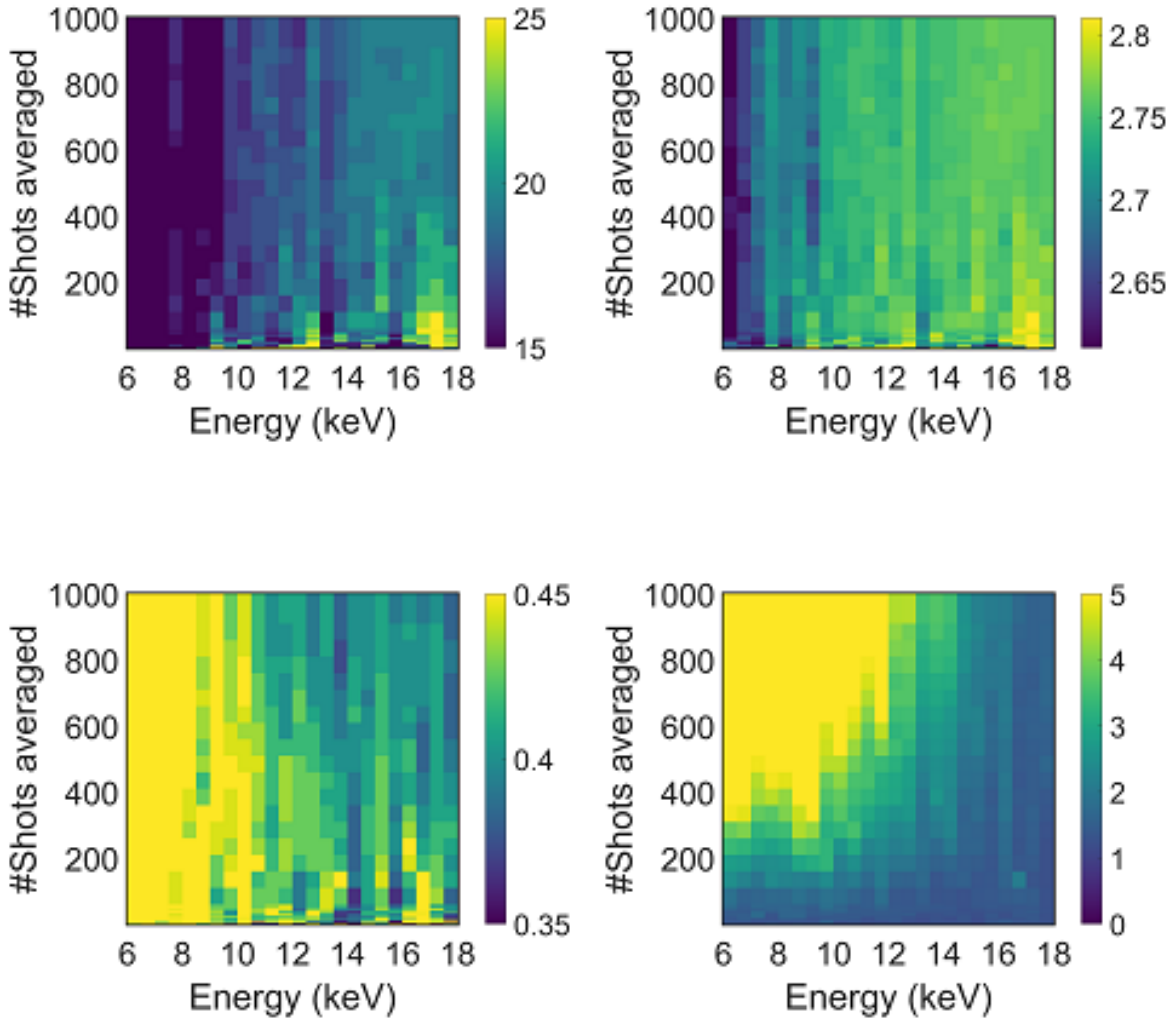


Figure 10. The best fit 2D maps found from modelling the difference signal with the incomplete model. Top-left: Excitation fraction. Top-right: PtPt distance. Bottom-left: ΔT Bottom-right: χ^2

Summary and Conclusion

A TR-WAXS experiment has been simulated for X-ray energies ranging from 6 to 18 keV. Specifically the X-ray scattering of the ground and excited state of PtPOP was simulated and used to construct difference scattering signals. For each X-ray energy the difference scattering signals were compared to a set of parametrized complete and an incomplete models in a χ^2 framework and the parametric values of the model fits were tracked as a function of both the X-ray energy and the number of difference curves averaged. The purpose of this was elucidate to what extend a TR-WAXS study benefits from the access of high energy X-rays. Tracking the parametric values associated with the minimum χ^2 values allowed for the determination of the prediction power of the complete and incomplete model. The complete model served as a reference and did, unsurprisingly, not benefit from higher X-ray energies. However, as seen from Figure 8 the incomplete models ability to correctly predict the parametric values is dependent on the X-ray energy with higher X-ray energies enabling a more precise result though at a price of an increased uncertainty. The increased uncertainty is related to the pixel count for each Q value as seen in Figure 9 and may be dealt with by additional averaging of curves as evident from Figure 4 and 10. As opposed to the complete model the incomplete model does not include a cage contribution, a choice made as this has also been the case for several experimental TR-WAXS studies. This is in part due to the solvent cage only being a decade or so old concept for which a complete understanding and unified method for its calculation is still an ongoing quest. The incomplete models ability to correctly predict the parametric values when using high energy X-rays enables the extraction of the true solvent cage signal and with it brings an opportunity to provide direct feedback of the cage signal to computational chemists.

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Paper X

Ultrafast dynamics in photoexcited iron-Carbene molecules.

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Ultrafast Dynamics in Photoexcited Iron-Carbene Molecules - an X-ray Study

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Abstract

Abstract

Introduction

- Motivate with solar cells, Ru is expensive, CAB2 has promising properties (long MLCT lifetime, ref. 2013 Tobias article).
- Here, we directly address the interplay between electronic and structural degrees of freedom and how energy is redistributed on external and internal degrees of freedom.

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[†]Unknown University

[‡]Second University

[¶]A shared footnote

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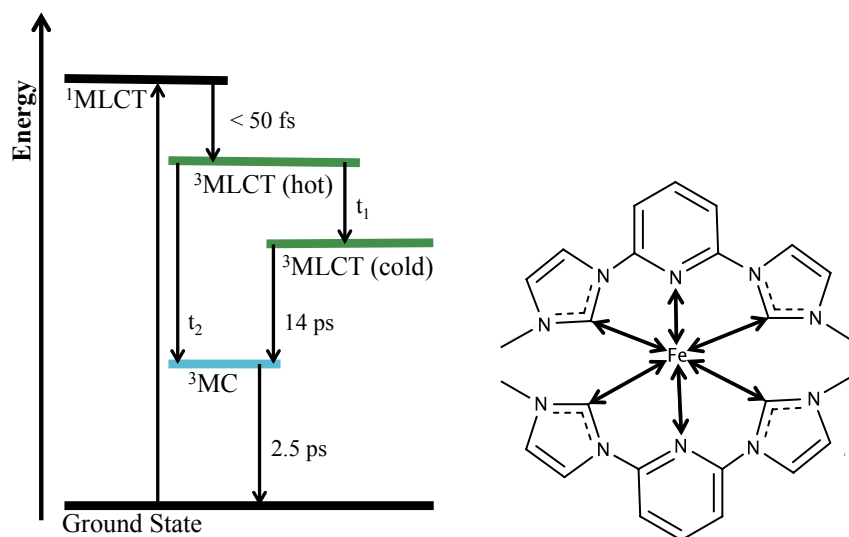


Figure 1: Left: Jablonski Diagram of the electronic processes of CAB2 as reported in ref.[?] Upon photoexcitation an electron is promoted from the iron center onto a ligand centered orbital which brings CAB2 into an MLCT state. The electron then returns to the iron center through non-radiative processes which brings CAB2 into an MC excited state. Right: Illustration of CAB2. Wavepacket oscillations occur on the ^3MC potential energy curve as indicated by the black arrows. The DFT results presented in ref.¹ suggest an Fe-ligand distance of 1.98 Å and 2.04 Å for the $^3\text{MLCT}$ and ^3MC states respectively.

Experimental Approach

Figure 1 presents a Jablonski diagram of the decay processes of CAB2 upon photoexcitation based on the results presented in ref.[?] Three excited states are expected to be populated: two metal-to-ligand-charge-transfer ($^1,^3\text{MLCT}$) states where the promoted electron is localised on the ligands, and one metal-centered (^3MC) excited state where the promoted electron has returned to the iron center.

The lifetimes of all three states are in the picosecond or sub-picosecond time range which motivates investigating them at an X-ray free electron laser facility. The measurements presented here were performed at the XPP end station at the Linac Coherent Light Source in August 2015, which enabled the application of 40 fs long 8 keV X-ray pulses.

The X-ray pulses proved a 20.3 mM solution of CAB2 in acetonitrile. The sample was studied in a 50 μm liquid jet at a sufficient flow rate to ensure full sample replenishment

between each successive X-ray pulse. The sample was pumped by a 50 fs long 400 nm optical laser pulse, which was focused onto a 120 μm spot size at the sample. By varying the delay between pump and probe pulses, a series of LUDHFLS snapshots was obtained which enabled a tracking of the time evolution of CAB2 upon photoexcitation. These snapshots were sorted and exposed to an extensive data reduction performed with similar methods as in described in ref.² Finally, the data was binned into 10 fs bins which is much shorter than the total experimental time resolution of 99 fs as reported in ref.⁷

During the experiment, X-ray emission spectroscopy (XES) and X-ray diffuse scattering (XDS) were measured simultaneously. XDS allows a structural analysis of the excited states while XES is sensitive exclusively to the electronic changes of the iron center. Furthermore, XDS offers additional information about the photoinduced changes in the solvent and in the interaction between solute and solvent. The XES results were recently published in ref.⁷ These results have been directly applied in the analysis of the XDS which is presented here.

Figure 2 shows the reduced difference XDS signal between the pumped and unpumped signal as a function of time delay between laser and X-ray pulse. The difference XDS signal shows a rapid grow-in at time zero when the photocycle is initiated. During the subsequent picoseconds the signal evolves and oscillations are directly observed on the low-Q region during the first picosecond. This is further confirmed by a Fourier analysis of the first 1.65 ps of the difference signal between 1.2 $\text{\AA}^{-1}$ and 1.6 $\text{\AA}^{-1}$ which shows a distinct peak at 285 ± 2 fs, that has been found from a Gaussian fit [SI].

Results and discussion

Kinetic Analysis

Based on figure 1, the lifetime of the $^1\text{MLCT}$ state is much lower than the experimental time resolution, but the $^3\text{MLCT}$ and ^3MC states are expected to contribute to the difference XDS signal. Furthermore, the solvent is expected to heat when the photoexcitation energy

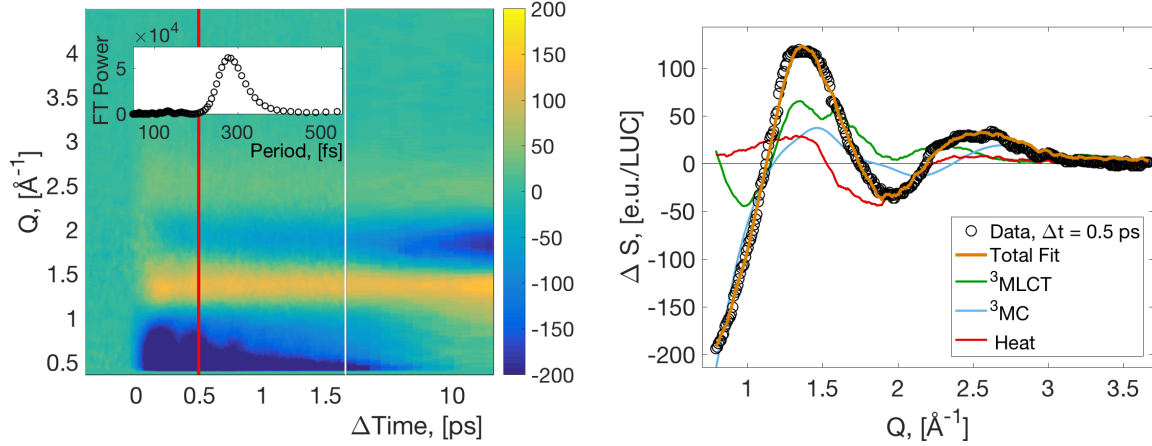


Figure 2: Left: The difference XDS signals between pumped and unpumped CAB2. The y-axis is the scattering vector, Q , while the x-axis shows the time delay between laser and X-ray pulse. Notice the transition to logarithmic time scale after 1.65 ps. The difference XDS signal grows in at time zero where CAB2 is photoexcited and evolves during the subsequent picoseconds. The inset of the figure shows the Fourier transformation of the first 1.65 ps after photoexcitation between $1.2 \text{ \AA}^{-1}$ and $1.6 \text{ \AA}^{-1}$, which shows a distinct peak at $285 \pm 2 \text{ fs}$. The red vertical line marks the time bin which is illustrated in the left figure. Left: Difference scattering signal with a time delay of 0.5 ps and the total fit with contributions according to equation 1.

is transferred from solute to solvent which also generates an XDS signal. The contributions are added in a superposition and the amplitude of each parameter is fitted in a linear least square fitting framework.

$$\Delta S(Q) = \alpha_{\text{MLCT}} \Delta S_{\text{MLCT}}(Q) + \alpha_{\text{MC}} \Delta S_{\text{MC}}(Q) + \Delta T \frac{\partial S}{\partial T}, \quad (1)$$

where the scaling factors in front of the excited state contributions represent excitation fractions of the corresponding excited state. The scaling factor of the solvent term represents the temperature increase of the solvent.

Referring to the time scales presented in figure 1, all excited states are expected to have decayed after 100 ps in which case the only contribution to the difference XDS signal is the solvent heat. A reference heat signal of acetonitrile has been measured at the ESRF,³ but the 100 ps difference signal was not well reproduced by the reference measurement. Consequently, in the present analysis, the 100 ps data was used as a representative of the

solvent heat signal.

Following the analysis approach presented in ref.,⁴ the contribution from each excited state is divided into the contribution from the isolated solute and from the photoinduced changes in the interaction between solute and solvent, where the latter is referred to as the cage term. In this way, the signal of each excited state, i is decomposed into

$$\Delta S_i(Q) = \alpha_i^{\text{solute}} \Delta S_i^{\text{solute}}(Q) + \alpha_i^{\text{cage}} \Delta S_i^{\text{cage}}(Q) \quad (2)$$

The two solute terms were obtained from DFT simulations presented in ref.¹, and the ³MC cage signal was simulated with classical molecular dynamics with the methods presented in ref.⁵ as discussed in detail in SI. In this way, the only contribution which is unknown is the ³MLCT cage term. Based on this observation, the shape of the ³MLCT cage term was estimated from an SVD analysis of the residual of a fit of the remaining four parameters as discussed in further detail in SI. In the analysis, the scaling factor of the ³MLCT cage signal was fitted along with the other four scaling factors.

The structural difference between the ground state and the ³MLCT state is small which implies a weak difference XDS solute signal and consequently large uncertainty on this scaling factor. Thus in the analysis presented here, $\alpha_{3\text{MLCT}}^{\text{solute}}$ was fixed to the values derived from the XES analysis presented in ref.⁷ respecting the uncertainty estimates provided. The remaining four scaling factors were fitted without constraints.

In the analysis of the difference XDS data that is presented in figure 2 each time bin was fitted independently. In order to illustrate this, figure 2 contains a the fit of the 0.5 ps time slice along with the ³MLCT, ³MC and heat contributions. To simplify the figure, the contribution to each excited state is presented as the sum of the solute and cage contributions, but the scaling factors are fitted independently. An illustration of all five contributions is found in SI.

The scaling factors of the two cage terms display very similar kinetics and have two

distinct time scales which match well with the lifetimes of the $^3\text{MLCT}$ and ^3MC states. Based on this observation, the combination of the two cage terms is assumed to describe the total cage term, but the entanglement of the cage terms implies that the scaling factor of each cage term can no longer be assumed to be equal to the excitation fraction of the corresponding state. Consequently, the scaling factors are not included in the further analysis presented here.

Figure 3 shows the scaling factors of the two solute signals and the solvent heat with errors found from the diagonal elements of the covariance matrix. There is a delay of approximately 100 fs between the $^3\text{MLCT}$ and ^3MC states and a further delay of approximately 300 fs before the solvent heats. The delay between the two excited states indicate that solute molecules populate ^3MC state after photoexcitation to the $^3\text{MLCT}$ state in confirmation of figure 1. The delay of the temperature increase implies that the solvent is not directly photoexcited which would cause a steep increase at time zero. Assuming single photon excitations of the solute molecule, the energy released to the solvent would be expected to give rise to a 3 K temperature increase of the solvent [SI], and the 3.5 K temperature increase of the solvent after 20 ps thus indicates the occurrence of multiphoton excitations of CAB2.

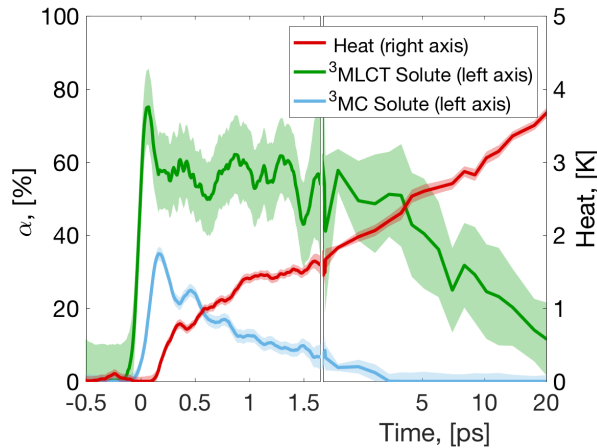


Figure 3: Excitation fractions of the two excited states (left y-axis) and the temperature increase of the solvent (right axis) according to equation 1. Errors on all three amplitudes are marked by shaded areas. The vertical lines marks the transition from linear to logarithmic time scale.

Structural Analysis

The population of an antibonding e_g orbital in the ^3MC state of CAB2 would expect to give rise to a sudden increase in bond length followed by vibrations as observed in related compounds such as $[\text{Co}(\text{terpy})_2]^{2+}$ ⁴ and $[\text{Fe}(\text{bpy})_3]^{2+}$.⁶ XDS is primarily sensitive to structural changes between the iron center and the ligands and one would therefore expect the Fe-ligand bond length to offer a good parametrization of any vibrations in CAB2 observed with XDS.

A theoretical DFT study of the most likely vibrational modes of CAB2 was published in ref.⁷ The breathing mode vibration of 297 fs oscillation period best matches the observed 285 ± 2 fs oscillation period which was found in the Fourier analysis presented in figure 2. Consequently, the CAB2 structure was varied from the equilibrium ^3MC structure in a breathing-like mode, where each ligand was divided into three ligand units consisting of a ring and possible sidegroup. The bond lengths within each ligand group were fixed and only the bond lengths between the ligand units and the iron center were varied. Consequently, the structural variations of the breathing-like mode are well parametrized through variations in the iron-ligand distance.

In figure 3, the oscillations are described by $\alpha_{3\text{MC}}$ which shows the strong correlation between structure and excitation fraction that were also seen in $[\text{Co}(\text{terpy})_2]^{2+}$.⁸ In order to include the oscillations in a structural analysis $\alpha_{3\text{MC}}$ is assumed to follow the overall decay following the method presented in ref.⁴ An exponential decay has been fitted and in the structural analysis described below, $\alpha_{3\text{MC}}$ has been fixed to these fit values respecting the uncertainty estimates. In order to account for the experimental resolution, the exponential signal was convoluted with a Gaussian.

The remaining four scaling factors were fixed to the values determined from the kinetic analysis respecting the uncertainty estimates, and thus only the ^3MC structure was fitted without constraints. The structure was fitted independently to each time bin in a maximum likelihood framework and the uncertainty on the fit was determined as the structure where

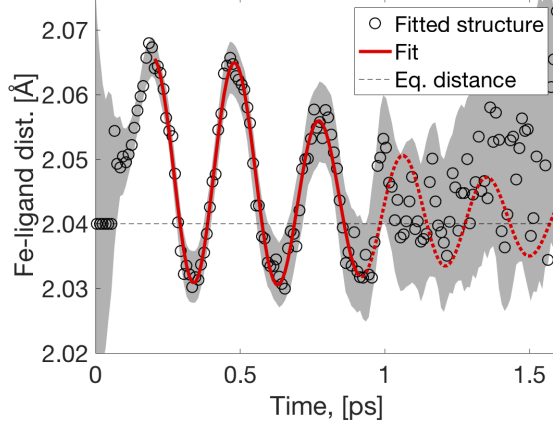


Figure 4: Fitted iron-ligand distance of ^3MC structure. The error on the distance has been found from the unreduced χ^2 and thus it increases drastically when the oscillations lose coherence after approximately 0.9 ps. A kinetic fit according to equation 3 yields an oscillation period of 290 ± 6 fs and amplitude 0.035 ± 0.003 Å. The fit has been drawn in a dashed line outside the fitting range.

the unreduced χ^2 had increased by 1 as further discussed in SI.

Figure 4 shows the fitted structure of each time bin parametrized through the iron-ligand distance of the ^3MC state. At time zero, the ^3MC state was not yet fully populated and the best fit structure thus appears random, which is also reflected by the large uncertainty. Consequently, the structural variation from the ^3MC state has been set to zero before 200 fs, where the ^3MC state is populated.

To further quantify the vibration, an oscillating signal with a background has been fitted to the structural variations. The background describes vibrational cooling in an anharmonic potential which is here approximated by an exponential decay. In order to account for the experimental resolution, the signal was convoluted with a Gaussian with a fixed width determined from the analysis of the XES data presented in ref.[?]

$$f(t) = H(t - t_{\text{XDS}}) \left(A \exp \left(-\frac{t - t_{\text{XDS}}}{\tau_1} \right) + B \exp \left(-\frac{t - t_{\text{XDS}}}{\tau_2} \right) \cos \left((t - t_{\text{XDS}})\omega + \phi \right) \right). \quad (3)$$

The fit yields an oscillation period of 290 ± 6 fs which is in excellent agreement with the results of the Fourier analysis and the theoretical simulations of ref.⁷

A vibrational amplitude of 0.035 ± 0.003 Å was found from the fit, which is approximately 1.8 % of the total bond length, and thus only vibrations near the bottom of the potential energy curve is observed. XDS observes the average of the wavepacket distribution, in which case the wavepacket tails can extend far from the bottom of the potential energy curve.

After approximately 900 fs the oscillations suddenly disappear and the uncertainty of the structure drastically increases. This abrupt loss of coherence is thought to reflect that the probability of transition between different vibrational modes of the ³MC potential energy curve is not yet constant in time.

Conclusion

Figure 5 summarises the results presented here. A kinetic analysis of the XDS data has been performed which has led to the confirmation of the DFT simulated structure of the ³MC state as reported in ref.¹ Furthermore, the ³MC structure has been fitted in a structural analysis which has enabled the description of a molecular vibration with a 290 ± 6 fs oscillation period in CAB2 in excellent agreement with a DFT predicted vibrational mode as reported in.⁷

References

Acknowledgement

Please use “The authors thank ...” rather than “The authors would like to thank ...”.

Supporting Information Available

A listing of the contents of each file supplied as Supporting Information should be included.

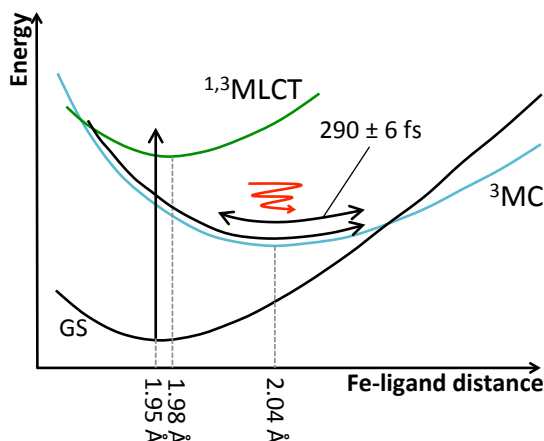


Figure 5: Sketched Franck-Condon diagram based on calculated potential energy curves¹ with the obtained iron-ligand distances marked. Initially, CAB2 is photoexcited which promotes an electron from the iron center onto the ligands and brings CAB2 into a $^{1,3}\text{MLCT}$ state (green curve). The electron then returns to the iron center which brings CAB2 into a ^3MC state (blue curve). Wavepacket oscillations occur on the ^3MC potential energy curve with an oscillation period of 290 ± 6 fs and with an amplitude of 0.035 ± 0.003 Å. In the ^3MC state the system undergoes vibrational cooling, and after 900 fs the oscillations suddenly lose coherence.

This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Paper XI

Investigating the Interplay Between Electronic Configuration and Geometric Structure in Relation to Functionality of a Novel Iron Photosensitizer.

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Introduction

Results and Discussion

The molecular structures and UV/visible absorption spectra for CAB2 and CAB3 have previously been reported and discussed [Liu2013] and are shown in Figure 1. The key difference between the two complexes is the larger Fe-ligand distance for CAB3 due to steric hindrance caused by the bulky *tert*-Butyl sidegroups, which causes a reduced sigma-donation of the carbene moieties of the ligands, ultimately reducing the t_{2g}/e_g energy splitting of the Fe d-orbitals. This causes the MLCT absorption band of CAB2 to be blueshifted compared to that of CAB3.

The different levels of sigma-donation of CAB2 and CAB3 results in dramatically different excited state dynamics, according to previously measured transient optical absorption spectroscopy (TOAS) data [Liu2013]. CAB2 displayed a 9ps broad excited state absorption (ESA) band, typically associated with MLCT states [ref], whereas a similar band for CAB3 was only observed for ~ 300 fs. The MLCT-like state of CAB2 decayed directly back into the ground state, whereas CAB3 transitioned through a 230 ps dark state, assigned to 5MC , which is typically observed for Fe(II) complexes [refs]. It was concluded that the stronger sigma-donation for CAB2 had destabilized the 3MC and 5MC states, increasing the lifetime of the MLCT state. This hypothesis was afterwards supported by quantum chemical calculations, which showed significant destabilization of the MC states [Fredin2014][Papai2016]. In the investigation of electron injection from $Fe(CNC-COOH)_2$ to TiO_2 [Harlang2015], the broad ESA band was unchanged upon injection and thus had to originate from electron loss from the Fe-center, rather than population of the ligand orbital. With this in mind, we measured TOAS of the two compounds once again, with resulting data shown in Figure 2. Singular value decomposition (SVD) was used to identify significant spectral components and their associated dynamics. For CAB2, two significant components were obtained, the first describing the ESA and ground state bleach (GSB) of the excited state(s) and a second corresponding to a spectral shift which can be assigned to vibrational cooling of the excited state [ref?]. For CAB3, the dataset is described by one significant component. Fitting the excited state decay of CAB2 with a single exponential decay results in a 9ps lifetime, in agreement with previous results [Liu2013]. The discrepancy between fit and data, however, indicates the presence of several excited states, and by including a second exponential component, the fit improves significantly, yielding lifetimes of 1.8ps and 13.8ps, with relative yields of 33% and 67%, respectively. For CAB3...

Following the commissioning of the first hard X-ray free electron lasers, X-ray emission spectroscopy (XES) probing the k-beta line has been established as an efficient technique for identifying charge and spin configurations of short-lived intermediate states of transition metal complexes [Zhang2014][Kjaer2016][other refs?]. In short, each combination of oxidation state and multiplicity is associated with a different shape and position of the XES spectrum. This can be used to identify oxidation states and multiplicities of excited states, by comparing a measured XES spectrum with reference spectra obtained from compounds with known oxidation states and multiplicities. It has been shown that Fe XES spectra can also be slightly influenced by the covalency of the Fe-ligand bonds [ref], and that modelling of the data can be optimized by creating linear combinations of reference spectra with different covalencies [Kjaer2016].

For time-resolved pump/probe measurements, laser ON – laser OFF difference signals are measured. The expected excited state signals can be calculated by subtracting the ground state spectrum from each excited state spectrum to yield the difference spectra shown in Figure 3. By fitting these reference spectra to a time-resolved dataset, the charge and spin configurations of the excited states can thus be identified. As this technique is only sensitive to the electronic configuration on the metal center[refs?], the 1MLCT and 3MLCT states cannot be distinguished, and will thus be denoted as 1,3MLCT.

A challenge of using k-beta XES to study spin cross over Fe(II) complexes, is the spectral similarities between the 3MLCT and 3MC state, as depicted in Figure 3. Here it is crucial to take the signal amplitude into account, as this is roughly twice as high for the 3MC compared to the 3MLCT. In this work, we overcame this issue by calculating the time-dependent excitation fraction, $\alpha(t)$, by convoluting the TOAS-determined excitation fraction with the IRF of the XES experiment and by scaling the amplitude to the initial excitation fraction of the XES data, assuming initial excitation to the 1MLCT state. With a predetermined excitation fraction, the relative population of the excited state species, 1,3MLCT, 3MC and 5MC was extracted by fitting the following equation to the difference XES data at each time point, t :

$$\Delta I(E) = \alpha(t) * ((1-x_1) * \text{MLCT}(E) + (x_1 - x_1 * x_2) * \text{3MC}(E) + (x_1 * x_2) * \text{5MC}(E))$$

Here x_1 and x_2 are the fit parameters describing the 1,3MLCT->3MC and 3MC->5MC transitions respectively, such that $\alpha_{\text{MLCT}}(t) = 1-x_1$, $\alpha_{\text{3MC}}(t) = x_1 - x_1 * x_2$, and $\alpha_{\text{5MC}}(t) = x_1 * x_2$.

The results of these fits are shown in Figure 4. In the top panels, difference spectra for a few selected time delays are shown for the two compounds.

Conclusions

References

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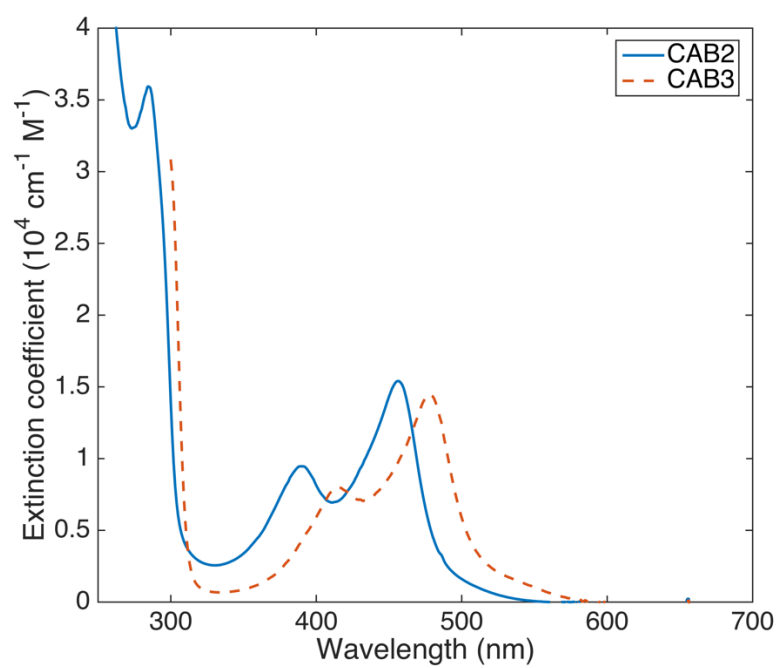


Figure 1 - Molecules and abs spec

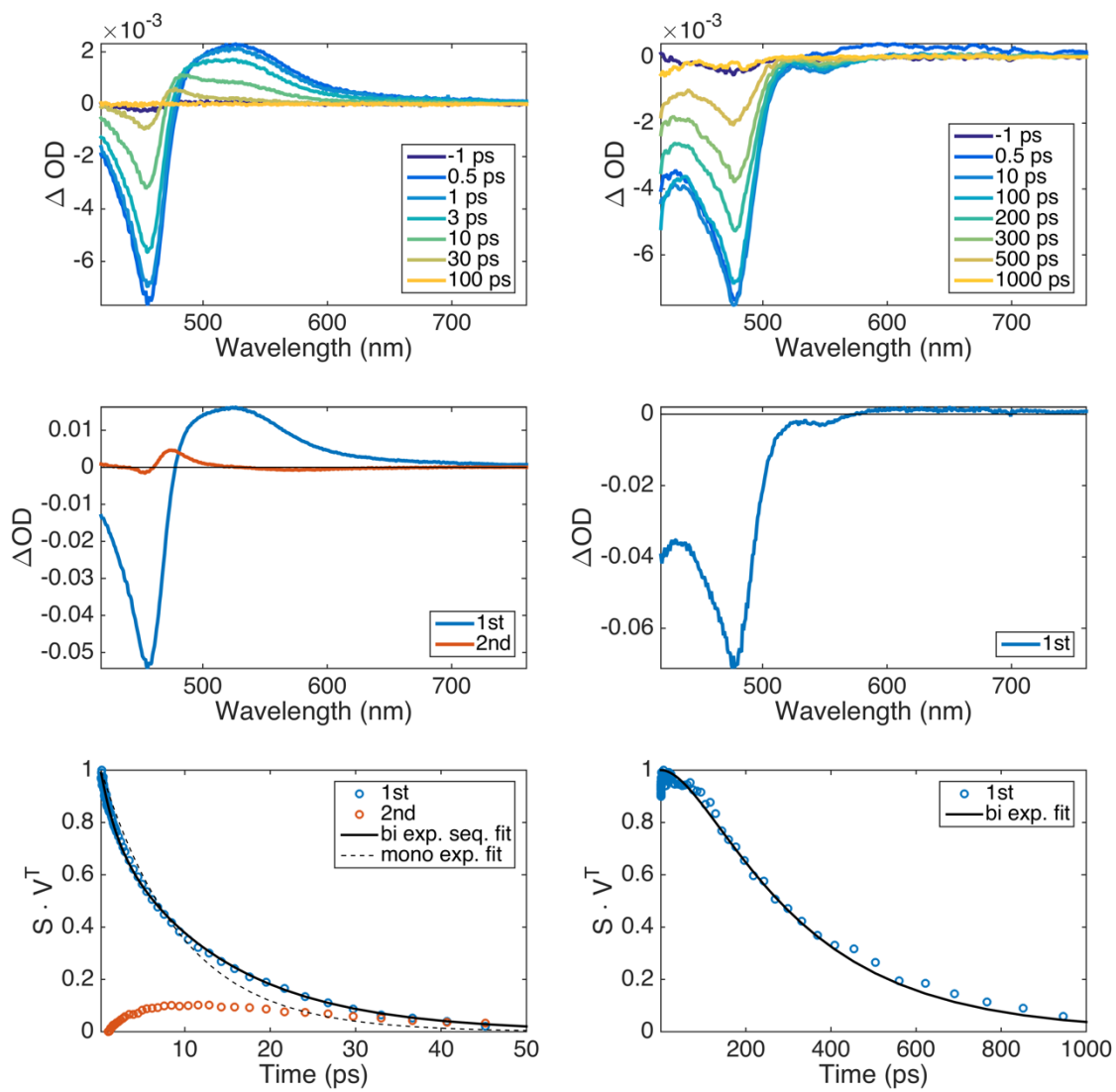


Figure 2

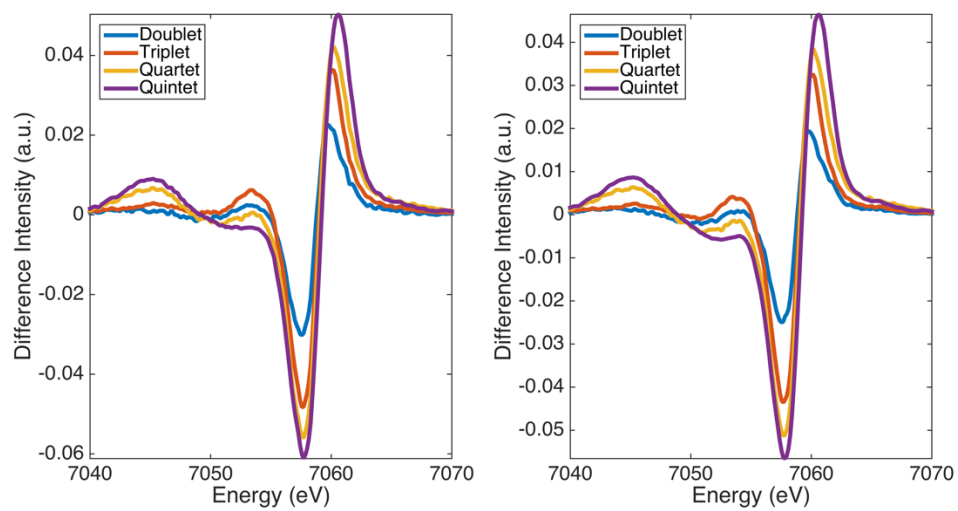


Figure 3 – *k*-beta ref spectra

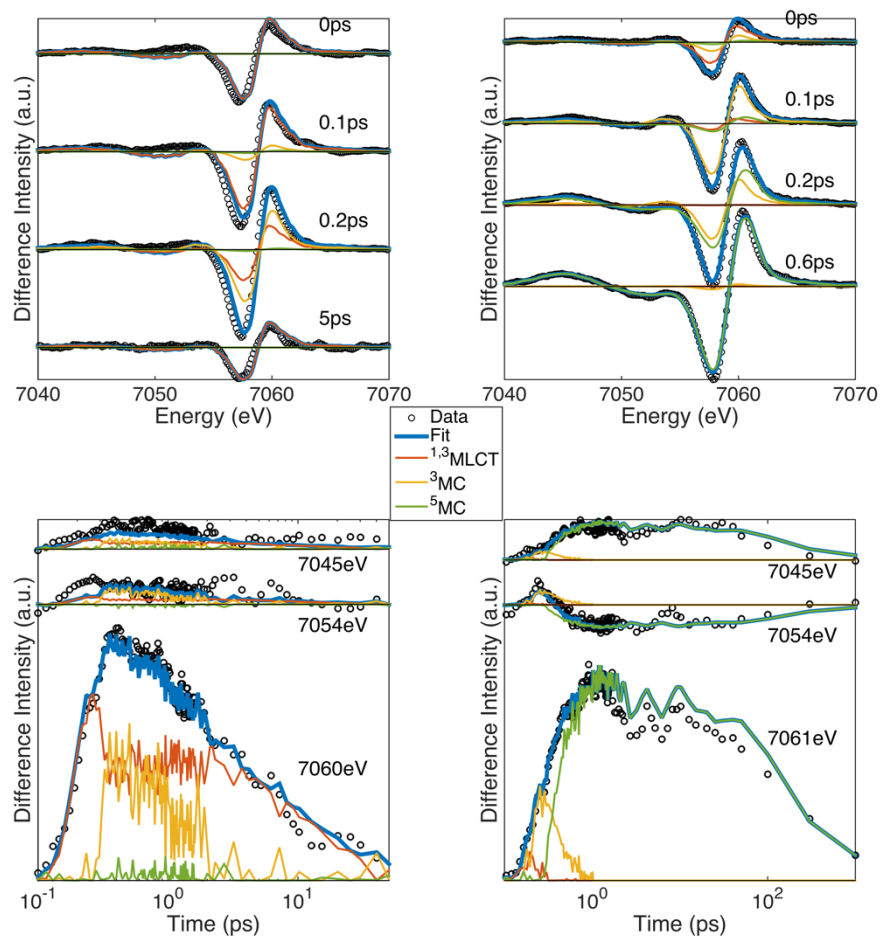


Figure 4

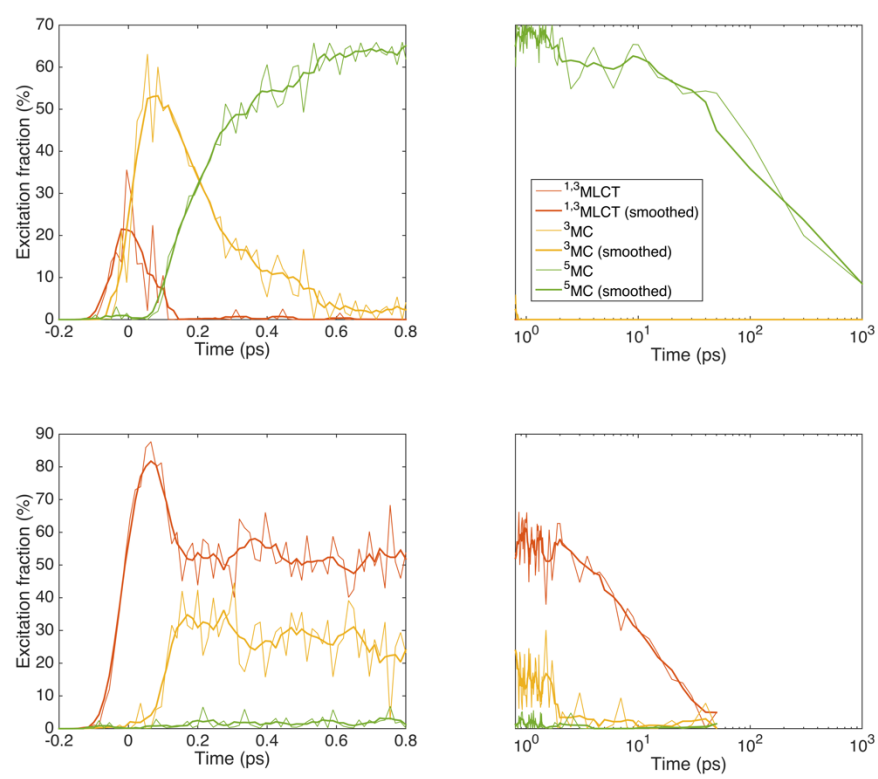


Figure 5