Picosecond Time-Resolved X-Ray Absorption Spectroscopy of Solvated Organometallic Complexes

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Abstract

We describe an experimental setup, which measures transient chemical changes of photoexcited solutes in disordered systems via time-resolved X-ray Absorption Spectroscopy (XAS) with picosecond temporal resolution. The setup combines a femtosecond amplified laser with picosecond X-ray pulses at beamline 5.3.1 at the *Advanced Light Source* in Berkeley, USA. New results on time-resolved XAS used for probing both the electronic and the geometric modifications of a photoexcited tris-(2,2'-bipyridine) ruthenium (II), $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ in water solution are presented.

1. Introduction

With the advent of time-resolved optical spectroscopy and the rapid development of femtosecond lasers, it has become possible to monitor the transient chemical changes occurring during an ongoing chemical reaction on fundamental timescales, which range from femtoseconds for molecular vibrational motions up to nanoseconds and microseconds for slower diffusion-controlled processes. In addition, since all chemical reactions take place on the atomic level, the complete study of transient chemical structures requires both ultrafast temporal resolution and atomic-level spatial resolution, usually in the picometer range. Femtosecond laser spectroscopy provides the necessary time-resolution to observe fully the photoinduced time evolution of a chemical system under investigation however it is less sensitive in detecting transient molecular structures.

On the other hand, there are many well-established structure-sensitive experimental techniques, such as Electron Diffraction, X-ray Absorption Spectroscopy (XAS) and X-ray or Neutron Diffraction, which are useful in determining the structures of complex many-body systems with atomic-level spatial resolution. Therefore, combining the advantages of ultrahigh atomic-level resolution and ultrafast temporal resolution of these techniques, one could visualize nuclear and electronic motions during the chemical reaction and capture the transient molecular structures. Among these structural tools, XAS offers distinct advantages, when applied to chemical and biological systems in the condensed phase. It is element specific and allows the measurement of the local electronic structure of an atom of interest in a disordered medium, such as a liquid, by X-ray Absorption Near Edge Structure (XANES) and the local geometric structure, including nearest neighbor distribution and relevant bond distances, by Extended X-ray Absorption Fine Structure (EXAFS).

Ultrafast Time-Resolved X-Ray Absorption Spectroscopy is a novel experimental technique which has not found wide-spread use yet. Although this scheme was originally proposed many

years ago [1–3], up to now, only a few time-resolved XAS measurements were carried out successfully, both in liquid [4–9] and gas phase systems [2] with nanosecond or longer temporal resolution. Only recently, Chen *et al.* [10] carried out a sub-nanosecond measurement of structural dynamics of an excited Copper (I) Diimine complex using both XANES and EXAFS and we reported on picosecond time-resolved XANES studies of a Ruthenium (II) tris-bipyridine complex in water solution reaching the sub-100 picosecond pulse-limited time resolution [11].

In our laser-pump X-ray-probe experiment, a femtosecond laser pulse starts a chemical reaction and a delayed X-ray pulse probes the photoinduced changes in a system. In full analogy to a laser-only experiment, by scanning the time delay between pump and probe pulse one can observe the time evolution of the transient chemical species. Synchrotrons are currently the brightest and the most stable pulsed X-ray sources. Moreover, they produce radiation that can be tuned over an extremely broad range up to the hard X-ray regime, e.g. hundreds of keV, however, the delivered X-ray pulse widths are usually limited to the tens of ps range, except for recent breakthrough experiments carried out by Schoenlein *et al.*, where a successful experimental scheme providing femtosecond synchrotron pulses was realized [12].

The feasibility of time resolved XAS depends on the number of available X-ray photons per data point. This depends on the X-ray pulse intensity and on the repetition rate of the measurement, which is typically in the 1 kHz range, when using femtosecond amplified lasers. On the other hand, synchrotrons operate at much higher repetition rate of usually 100–500 MHz, which means that after synchronization of both sources we reduce the available X-ray photon flux by more than 5 orders of magnitude. Therefore, these experiments require a very sensitive detection scheme given that the X-ray pulse intensity at 3rd generation X-ray beamlines is rather weak, i.e. 10^4 – 10^6 photons/pulse. Furthermore, there are other experimental challenges imposed by the nature of the experiment itself and a careful optimization of the sample geometry is required. The details on both sample and detection scheme optimization can be found elsewhere [13].

2. Experimental Setup

The experiments are carried out at bend magnet beamline 5.3.1 of the *Advanced Light Source* in Berkeley, USA, which operates between 2.5 and 12 keV. We use a special filling pattern of the storage ring called *camshaft mode* (Fig. 1). It consists of a close-packed multibunch train followed by a 100 ns empty section, in which a ten-fold more intense single electron bunch is placed, whose radiation we use in the pump-probe measurement. The beamline provides a hard X-ray photon flux of about

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Fig. 1. The ALS storage ring filling pattern (left). The single electron bunch, so called *camshaft pulse*, is placed in a 100 ns empty section and thus is well separated from the 600 ns long multibunch. The X-ray radiation resulting from this bunch provides us with 60–80 ps single X-ray pulses at 1.52 MHz repetition rate used in our experiments (top right). The 200 fs laser pulse at 1 kHz repetition rate is synchronized to one of these camshaft pulses with fixed time delay (bottom right).

10^{12} photons/s (corresponding to ca. 10^4 photons/single X-ray pulse) with a spectral resolution of $3 \cdot 10^{-4}$ bandwidth around 3 keV energy range. The bend magnet radiation is imaged 1 : 1 via a grazing incidence Pt-coated mirror (5 mrad deflection) into the experimental X-ray hutch. A Ge (111) double monochromator with fixed output height selects X-ray photon energies between 2–12 keV. An X-ray chopper in front of the monochromator is set to 2 kHz repetition rate reducing the heat load on the first monochromator crystal. The experimental chamber is filled with atmospheric He gas in order to minimize transmission losses for radiation below 7 keV.

The laser source is a Ti: sapphire based amplified femtosecond laser system, which delivers 1.8 mJ, 200 fs, 800 nm laser pulses at a repetition rate of 1 kHz. Both sources, i.e. the laser and the storage ring, require stable and precise synchronization. The key factor in the synchronization scheme is locking of the laser oscillator frequency to the radio frequency (RF) of the storage ring with a stable phase. The oscillator timing is the most important step in this process, because its temporal precision defines the relative jitter between laser and X-ray pulses. Once the complete synchronization between laser pump pulses and camshaft probe pulses is properly set, the relative time delay between them can be kept fixed in order to scan the energy spectra at a given time instant after the photoexcitation or alternatively we can scan the time delay electronically (at a fixed X-ray energy) to record the temporal evolution of the transient X-ray absorption. The sample consists of a free-flowing liquid jet with a thickness of 100 μm . The amplified femtosecond laser pulses provide the photoexcitation source and they can be delivered at the fundamental wavelength of 800 nm, or frequency-doubled and tripled, namely 400 nm and 266 nm respectively. The amplified and frequency-doubled Ti: Sapphire laser at 1 kHz can currently deliver up to 550 μJ pulse energy at 400 nm.

The laser is focused on the sample down to ca. 300 μm diameter with its beam size being slightly larger than the X-ray focal size, which is $250 \times 90 \mu\text{m}$. The flow speed of the jet is adjusted in a way that we can always provide a fresh sample solution at the site where the photoexciting laser pulse arrives, i.e. the jet flow speed of 5 m/s ensures that after 60 μs the sample will move out of the probe focus. Spatial and temporal overlaps are secured in two steps. Initially, we align both X-ray and laser beams through

Fig. 2. Data acquisition scheme for recording time-resolved XAS. The X-ray pulses are recorded with a sensitive and suitably fast X-ray detector, i.e. avalanche photodiode, at 2 kHz repetition rate, which permits us to record *in situ* the unexcited and photoexcited sample on a shot-to-shot basis. The measured single X-ray pulse intensities are then fed into the gated integrator. The pair-wise subtraction of adjacent pumped (black) and unpumped (white) intensities yields the transient difference XAS spectra. The PC sorts the recorded data and controls both the X-ray monochromator and the laser-X-ray time delay settings.

a 50 mm pinhole at the sample position. Then we monitor at the sample position both pulses individually with a fast photodiode. This allows us to set the timing with a precision around 100 ps by comparing the rise times of both signals. After this procedure, we place the sample within both beams and measure a photoinduced signal to fine tune both spatial and temporal overlap.

The transmitted X-ray pulse train is detected using an avalanche photodiode (APD) as an X-ray detector, which resolves the single X-ray pulse intensities and camshaft pulses can be resolved and detected yielding the output signal of about 10 ns (FWHM), as shown in Fig. 2. The APD signal is amplified by a fast pre-amplifier and subsequently plugged into a gated integrator. The gate of the integrator is set to this 10 ns width for an optimum signal-to-noise ratio. The single X-ray pulse intensities are then recorded at twice the laser repetition rate, i.e. 2 kHz, which means that we acquire simultaneously transmitted camshaft pulse intensities originating from laser-pumped and unpumped species. Later on, the subtraction of adjacent pairs of X-ray pulse intensities yields the transient difference XAS in transmission mode. Using the described data acquisition strategy cancels out any noise contributions and electronics drifts at frequencies lower than 1 kHz for a given pump-probe difference signal. Moreover, this difference detection scheme reduces our susceptibility towards gradual sample deterioration due to extended exposure to radiation, since we always measure the unexcited sample every 0.5 ms before probing the photoinduced changes and thus long-term changes in the sample do not contribute to our difference signal. One interesting prospect of our detection scheme is that we can envision studying of non-cyclic photochemical reactions without contaminating our pump-probe spectra with the overall change in XAS due to sample degradation.

With the above-described detection strategy, we are able to record high precision and quality XAS spectra. In fact, careful noise analysis shows that our current sensitivity has reached 90% of the shot-noise limit of the X-ray source. It is illustrated in Fig. 3a, which shows the pulse height distribution of 10^4 recorded single X-ray pulse intensities. From this distribution, we can

Fig. 3. a) Pulse height distribution of 10^4 recorded single X-ray pulses at a fixed energy without laser. In our data acquisition scheme we record the averaged value $\bar{S}$ together with its standard deviation σ_S for a given number of single X-ray pulses. b) On the left ordinate (stars), the averaged readout voltage is plotted as a function of stored current in the single electron pulse. The right ordinate (circles) corresponds to the effective number of recorded photons, according to relation (1), plotted as a function of the same value of the single bunch current. We find the linear response of the utilized detection scheme and very good agreement between measured pulse height distribution and the effective number of single X-ray pulse photons.

estimate an effective number of monochromatic X-ray photons per pulse, via the equation:

$$N = \left(\frac{N}{\Delta N} \right)^2 = \left(\frac{N}{\sqrt{N}} \right)^2 \geq \left(\frac{\bar{S}}{\sigma_S} \right)^2 \quad (1)$$

with N being the average number of photons per pulse, $\Delta N = N^{1/2}$ being the standard deviation or shot noise distribution of the X-ray source, $\bar{S}$ denotes the averaged measured signal height (in Volts), and σ_S the measured standard deviation (in Volts) of the pulse height distribution. Of course, this relation holds only if σ_S contains no other contributions, e.g., electronic noise. On the other hand, using Eq. (1) we can estimate the number of photons per X-ray pulse and compare it to the calculated value for the beamline (at the given X-ray energy) where the experiment is carried out.

The beamline is specified to deliver ca. 1×10^{12} photons/(s $\times$ 0.1% bandwidth) at 2.8 keV for 400 mA of stored current. At this beam current value, the camshaft current amounts to 10 mA, which corresponds to 1.65×10^4 camshaft photons/pulse and 0.1% bandwidth. Due to the fact that we only use 0.03% of the available bandwidth, the corresponding number of X-ray photons on the sample scales down to ca. 5000 photons/pulse. Taking into account the transmission through the sample (10%) and through Be filters (70%), we obtain a value of 350 photons per pulse incident on the X-ray detector at 10 mA of camshaft current, and this is very close to the value measured via the pulse height distribution of single recorded X-ray pulses (Fig. 3b).

3. Results and discussion

With the above-described experimental setup, we have investigated the photoexcited Metal-to-Ligand Charge Transfer (MLCT) reaction of aqueous tris-(2,2'-bipyridine) ruthenium (II), $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$. Its excited state properties have been extensively studied with optical spectroscopy [14–18], nevertheless, still little is known about its excited state structure, which can be investigated via time-resolved XAS. The photoexcitation cycle (which is completed on a sub-microsecond time scale) is displayed in Fig. 4. Light absorption by $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ results in the formation of a Franck-Condon MLCT singlet excited state, $^1(\text{MLCT})$, which undergoes sub-picosecond intersystem

Fig. 4. Photoexcitation cycle of the solvated reactant species in its singlet ground state leads to formation of an intermediate triplet excited state of $[\text{Ru}^{\text{III}}(\text{bpy}^-)(\text{bpy})_2]^{2+}$, which radiatively returns to the initial reactant state after ca. 300 ns.

crossing to a long-lived triplet excited state, $^3(\text{MLCT})$ [17], with near-unity quantum yield. In the process, the D_3 symmetry of ground state $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ is reduced to C_2 symmetry of $[\text{Ru}^{\text{III}}(\text{bpy}^-)(\text{bpy})_2]^{2+}$ in the $^3(\text{MLCT})$ state. This reaction involves a change of oxidation state of the Ru central atom, which can be probed by monitoring the XANES region around the ruthenium L_3 -edge. Indeed, oxidation states of (ground state) Ru^{II} and (photoexcited) Ru^{III} complexes exhibit clear differences in their L-edge XANES [19–21]. This can be seen in Fig. 5a around the Ru L_3 edge. A pre edge absorption feature at 2841.0 eV (denoted B in Fig. 5a) characterizes the bivalent compounds due to the $2p_{3/2} \rightarrow 4d_{3/2}(\text{e}_g)$ transition [19], next to the weaker $2p_{3/2} \rightarrow 5s_{1/2}$ transition around 2851 eV (feature C) [20]. Removal of the weakest bound electron from the fully occupied $4d_{5/2}(t_{2g})$ level generates a trivalent ruthenium compound [19], opening up additional absorption due to the allowed $2p_{3/2} \rightarrow 4d_{5/2}(t_{2g})$ (feature A') in addition to an oxidation state induced shift [19]. Thus we observe the appearance of the A'/B' doublet structure in the trivalent L_3 XANES together with the energetic $B \rightarrow B'$ and $C \rightarrow C'$ shift (Fig. 5a), resulting from the change of oxidation state of the Ru central atom and formation of $^3(\text{MLCT})$ (see Fig. 4).

The recorded transient difference absorption spectrum is shown on Fig. 5b. It is plotted as a function of the X-ray probe energy E , recorded 50 ps after laser excitation (data points with error bars) for a sample containing 80 mmol/l solution of

Fig. 5. (a): Static L₃-edge X-ray absorption spectrum of ground state [Ru(bpy)₃]²⁺ (black trace, measured 0.5 ms before the laser strikes the sample), and excited state absorption spectrum (red dots) generated from the transient data curve T in (b) via Eq. (2). (b): Transient X-ray absorption spectrum of photoexcited aqueous [Ru(bpy)₃]²⁺ measured 50 ps after laser excitation.

[Ru^{II}(bpy)₃]²⁺ in H₂O. This transient contains all the electronic changes from the reactant state absorption spectrum, $R(E)$, to the product state absorption spectrum, $P(E, t)$, at the time t after photoexcitation can be expressed by the following relation:

$$T(E, t) = f(t) \cdot [P(E, t) - R(E)], \quad (2)$$

with $f(t)$ being the fraction of excited state species at time t . Therefore, one can directly access the XANES spectrum of the product state from the measured transient signal and the reactant state XAS, provided that the $f(t)$ value is known. Alternatively, one can derive $f(t)$, if the exact shape of the product state XAS, $P(E, t)$ is given. From laser-only measurements we know that the photoexcitation yield of the sample is ca. 10%, but here we have treated the data differently: Assuming no change in oscillator strength for the B feature, we have constructed the product state spectrum $P(E, \Delta t = 50 \text{ ps})$ via Eq. (2) by adjusting $f(t)$, until features B and B' have equal amplitudes. This yields a value of $f = 10.4\%$ in close agreement with our prediction from the optical-only measurements. It contains an energetic shift of all features by 1.2 eV together with the photoinduced appearance of the A' feature, as expected. The $A'-B'$ splitting (4 eV) and the B'/A' intensity ratio (ca. 2.3) is indeed close to the values observed for [Ru^{III}(NH₃)₆]³⁺ complex, which has the same valency and a similar coordination symmetry (O_h versus D₃) as the bipyridine complex. Assuming no change in oscillator strength for the B feature in the ground and photoexcited states seems plausible, since the 4d_{3/2} (e_g) level should remain empty in both cases. In addition, the peak intensities of the B feature of ground state [Ru^{II}(bpy)₃]²⁺ and [Ru^{III}(NH₃)₆]³⁺, as compared in Ref. [11], are indeed very similar.

Fig. 6. Time delay scan between laser and X-ray pulses around time zero of photoexcited aqueous [Ru(bpy)₃]²⁺. Cross-correlation signal recorded between the 200 fs laser pulse and the 70–80 ps long X-ray pulse can be fitted with a Gaussian error function, which derivative is a Gaussian with a FWHM around 70–80 ps, which corresponds to the single X-ray pulse width.

Our experimental setup allows us also to vary the delay time between laser and X-ray pulses. As it is presented in Fig. 6, we scanned the time delay in 2 ps steps with the X-ray energy set near the maximum of feature B (ca. 2840 eV) thus allowing us to observe the appearance of the photoinduced bleach signal. Once the electron has been excited to the triplet MLCT state (in ca. 300 fs, [17]) we can observe the induced oxidation state change of the Ru central atom, and therefore the time evolution of this transient signal is entirely governed by the cross-correlation time of the laser and the X-ray pulses. Cross-correlation signal recorded between the 200 fs laser pulse and the 70–80 ps long X-ray pulse can be fitted with a Gaussian error function, which derivative is a Gaussian with a FWHM around 70–80 ps, which corresponds to the actual single X-ray pulse width provided by the ALS (depending on the stored charge in the single electron bunch). It should be stressed that our current temporal resolution is X-ray pulse-limited and our setup is prepared to be directly implemented into femtosecond-resolved XAS measurements given that ultrashort X-ray pulses could be provided. With this precise timing measurement, we can then set a fixed time delay with better than 10 ps accuracy. While this method serves as a convenient analog of conventional laser cross-correlation measurement for setting the correct time delay between the pulses, our setup can be exploited for measurements of kinetic traces out to several hundred of microseconds in a few picosecond steps.

In order to verify the limits of our experimental setup, we carried out a solute concentration dependence study. In fact, the 80 mmol/l sample concentration used to collect the data in Fig. 5 is rather high for typical photochemical studies, and gives rise to additional processes occurring on nanosecond time scales. Therefore, we decreased the concentration and repeated the measurement of its transient absorption. The results are shown in Fig. 7 for different concentrations down to 1 mmol/l and using an increased laser focus thus reducing the laser intensity (and the photoexcitation yield) in the overlap volume. The spectra represent single scans with 2 s accumulation time per data point except for the 1 mmol/l sample, which utilized 40 s. The corresponding error bars of the 1 mmol/l spectrum are ca. a factor

Fig. 7. Solute concentration dependence of the photoinduced aqueous $[\text{Ru}(\text{bpy})_3]^{2+}$. All data, except for 1 mM trace (solid line with open circles), were recorded at the same experimental conditions (laser intensity, data accumulation time, etc.). The arrow indicates the decreasing concentration of the sample. The lowest concentration sample was recorded at 20 times larger data accumulation time in order to improve the signal-to-noise ratio. All data were collected during single energy scan around Ru L_3 -edge (feature B) and measured 50 ps after laser excitation.

of 4.5 smaller than those of the other samples, which we expect from a shot-noise limited detection scheme. These measurements prove that we are capable of descending into significantly lower concentration regions without dramatic loss of signal-to-noise ratio. These results are very promising because one can envision the study of samples for which large concentrations are impossible to prepare.

Moreover, decreasing sample concentration rules out several unwanted effects, such as proximity effects of closely-packed excited species that can influence the ongoing photochemical reaction. In addition, biologically relevant samples are usually investigated in solutions with up to 1 mmol/l concentration, and hence we can imagine such studies in the near future. Furthermore, it should be remarked that these results were obtained in transmission mode. Another possible near-future extension of our technique could be the application of X-ray fluorescence spectroscopy, which is in principle background-free, and could bring another improvement in signal-to-noise ratio.

4. Conclusion

Time-Resolved X-ray Absorption Spectroscopy is a new technique, which permits the investigation of photoinduced processes on various chemical systems on time scales down to the cross-correlation time between the laser and the X-ray pulses. We have successfully applied this technique to investigate the photoinduced charge transfer reaction of aqueous $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ in both X-ray absorption energy and in time. This

result demonstrates the utility of current pulsed X-ray sources for future ultrafast XAS studies. Furthermore, we showed the high sensitivity of our technique, which allows measurements of very weak transient XAS signals with X-ray pulse-limited temporal resolution (currently in 60–80 ps range). With only ca. 10^6 photons per data point (corresponding roughly to 1 second accumulation time per data point in the range 3–10 keV), we have achieved a signal-to-noise ratio of ca. 20 for measuring the 10% amount of transient species via time-resolved XANES with sensitivity nearly corresponding to the shot-noise limit of the source.

Particularly promising are the prospects of carrying out time-resolved structural studies via EXAFS. The modified transient structure of the MLCT species has never been directly observed in experiment. Time-resolved EXAFS exploiting our new technique are feasible and could yield the individual Ru-ligand distances of the intermediate species for the first time. Our future work will focus on exploiting this structural tool to study nuclear rearrangements with picosecond temporal resolution.

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