Synchrotron ultrafast techniques for photoactive transition metal complexes

Elisa Borfecchia¹, Claudio Garino¹, Luca Salassa² and Carlo Lamberti¹

¹Department of Chemistry, NIS Centre of Excellence, University of Turin, via P. Giuria 7, 10125 Turin, Italy
²CIC biomaGUNE, Paseo Miramón 182, 20009 Donostia-San Sebastián, Spain

In the last decade, the use of time-resolved X-ray techniques has revealed the structure of light-generated transient species for a wide range of samples, from small organic molecules to proteins. Time resolutions of the order of 100 ps are typically reached, allowing one to monitor thermally equilibrated excited states and capture their structure as a function of time. This review aims at providing a general overview of the application of time-resolved X-ray solution scattering (TR-XSS) and time-resolved X-ray absorption spectroscopy (TR-XAS), the two techniques prevalently employed in the investigation of light-triggered structural changes of transition metal complexes. In particular, we herein describe the fundamental physical principles for static XSS and XAS and illustrate the theory of time-resolved XSS and XAS together with data acquisition and analysis strategies. Selected pioneering examples of photoactive transition metal complexes studied by TR-XSS and TR-XAS are discussed in depth.

1. Introduction

Light excitation of transition metal complexes induces electron density reorganizations and changes in their molecular structure that result in unique photophysical and photochemical properties that are highly sensitive to the chemical environment (e.g. solvent, reactants). In particular, solution-phase photoreactions are strongly influenced by the solute–solvent interplay. Here, the
reaction dynamics is not only determined by the potential energy surfaces of the reactant and product species, but also solvent molecules play a crucial role in defining the reaction pathway [1].

In the last few decades, the study of excited states (ESs) in metal complexes has been widely undertaken practically across all fields of chemistry involving metals. Applications span from solar energy conversion [2–4] and catalysis [5] to biology and medicine [6–9]. Significant advances in the comprehension of the ES dynamics of molecular systems have been achieved with the development of time-resolved optical techniques and, in particular, the advent of femtosecond laser sources has fostered unexpected possibilities for ultrafast spectroscopy [10,11].

Figure 1. Schematic representation of the pump-and-probe set-up for ultrafast characterization of photo-induced processes. Inset: a potential well diagram illustrating the light-matter interaction in a molecular system, after absorption of the pump pulse (GS, ground state; FC, Franck–Condon state; ES 1 and ES 2, first and second thermally equilibrated excited states; q, generalized molecular coordinate; E, system energy; magenta arrow, absorption of a pump photon; blue arrow, radiative decay channel; green arrow, non-radiative decay channel). (Online version in colour.)

Time-resolved laser spectroscopy relies on the application of the pump–probe scheme (figure 1), introduced in the late 1980s by Zewail—awarded for these pioneering studies with the 1999 Nobel Prize in chemistry [12]. A laser pulse is initially absorbed, triggering a photoreaction; subsequently, another pulse, generally lower in intensity, records the optical/vibrational response of the sample as a function of the time delay between the two pulses [13–17]. In this way, dynamics of the wavepackets in ESs [18,19], ES population and energetics can be obtained at the ultrafast time scale [20–23], with time resolution limited only by the shorter pulse duration [24,25].

Structural information is only indirectly accessible using optical/IR probe pulses. Their sensitivity is limited to valence electrons and vibrational features, respectively. On the other hand, direct insights into photo-induced structural dynamics can be achieved using ultrashort X-ray [25–28] or electron [29–32] probe pulses, which are nowadays available at synchrotron facilities and high-energy electron sources, respectively. Using this approach, it is possible to obtain a molecular movie of a given photoprocess, i.e. a series of temporal-ordered snapshots of the system structure. Because of the relatively low penetration depth of electrons [33,34], X-rays are more suitable for probing crystalline and liquid samples. Structural methods such as X-ray absorption spectroscopy, X-ray diffraction and X-ray scattering have been employed in the pump-and-probe
scheme for studying rearrangements of atoms, functional groups and portions of molecules in a variety of systems. As highlighted in §4, significant examples go from small molecules such as CH$_3$I and C$_2$H$_4$I$_2$ to metal complexes and photoactive haem proteins. Typical time resolutions reached in these studies are of the order of 100 ps, limited by the X-ray pulse duration. Such resolution, though missing the fs-scale coherent dynamics (e.g. relaxation from the Frank–Condon state, FC in figure 1, to the bottom of the ES$_1$ potential well), is enough to effectively monitor thermally equilibrated ESs (labelled ES$_1$, ES$_2$ in figure 1) and capture their nuclear coordinates as a function of time.

In the case of transition metal complexes, ES structures in solution have been captured using time-resolved X-ray absorption (TR-XAS) and X-ray solution scattering (TR-XSS), which are the subject of the present contribution. Herein, the basic principles of these two approaches will be described, and a general overview of the most exciting results obtained by TR-XAS and TR-XSS on the photophysics and photochemistry of metal complexes will be provided.

2. Time-resolved X-ray scattering: theoretical background

In this section, we first briefly discuss the physics of the X-ray elastic scattering process. We show how to derive very general equations, valid for both crystalline materials and less-ordered systems. Subsequently, we focus on the peculiarities of the X-ray scattering from non-crystalline samples, as amorphous solids and solutions. The fundamental mathematical instruments employed for data modelling in such cases are discussed, e.g. the Debye equation and the radial distribution functions (RDFs) formalism. Finally, we describe the ultrafast time domain, introducing TR-XSS. A brief overview on laser-pump/X-ray-probe experimental schemes adopted at synchrotron facilities and theoretical models developed to interpret TR-XSS data is provided.

(a) X-ray elastic scattering: basic physical principles

When an X-ray probe pulse arrives at the sample, a part of the incoming radiation is elastically scattered. Details on the quantum-mechanical theory developed to describe such a process can be found in the original reports by Wentzel [35] and Waller [36–38], as well as in later specialized literature [39–41]. Hereinafter, we have provided a synthetic discussion of fundamental concepts and key equations.

The amplitude of the scattered X-ray wave $A(q)$ is expressed by the following equation:

$$A(q) = \int \rho_e(r) \exp(-i q \cdot r) \, dr. \tag{2.1}$$

In equation (2.1), $q = k - k_0$ is the wavevector proportional to the momentum transfer ($\hbar = \frac{h}{2\pi}$) during the elastic scattering interaction as schematically represented in figure 2, where $k_0$ and $k$ are the incident and the scattered wavevectors, respectively. The X-ray scattering amplitude $A(q)$ and the sample electron density $\rho_e(r)$, expressed as a function of the three-dimensional coordinate $r$, are related by a Fourier transform relation, i.e. equation (2.1). This relation is of key importance and shows how the X-ray scattering signal is dependent on the sample structure.

However, we are experimentally limited to measure only the square modulus of the scattering amplitude $A(q)$, that is, the scattered intensity $I(q)$ expressed by the following equation:

$$I(q) = |A(q)|^2 = \left| \int \rho_e(r) \exp(-i q \cdot r) \, dr \right|^2. \tag{2.2}$$

Any information on the X-ray phase is unavoidably lost: this long-standing complication in crystallography is well known as the ‘phase problem’ [42]. As a consequence, it is impossible to apply directly the Fourier transform relation between $\rho_e(r)$ and $I(q)$ and therefore determine $\rho_e(r)$ from the measured $I(q)$. Nevertheless, the global electron density $\rho_e(r)$ can be expressed as a superimposition of the individual atomic electron densities centred in the nuclear positions $r_n$. 

In the case of transition metal complexes, ES structures in solution have been captured using time-resolved X-ray absorption (TR-XAS) and X-ray solution scattering (TR-XSS), which are the subject of the present contribution. Herein, the basic principles of these two approaches will be described, and a general overview of the most exciting results obtained by TR-XAS and TR-XSS on the photophysics and photochemistry of metal complexes will be provided.
Figure 2. Schematic representation of the elastic scattering process; \( \mathbf{k}_0 \) and \( \mathbf{k} \) are the incident and scattered wavevectors, respectively, while \( \mathbf{q} = \mathbf{k} - \mathbf{k}_0 \) is the vector describing the momentum transfer during the interaction and \( 2\theta \) is the scattering angle, and where \( |\mathbf{q}| = q = 2|\mathbf{k}_0| \sin \theta = 4\pi \sin \theta / \lambda \). (Online version in colour.)

equation (2.3), where \( \rho_n \) is the electron density of the \( n \)th atom and the vector \( \mathbf{r} \) describes a generic position from the origin of the reference system,

\[
\rho_e = \sum_n \rho_n (\mathbf{r} - \mathbf{r}_n). \tag{2.3}
\]

By combining equations (2.1) and (2.3), it is possible to express the scattering amplitude \( A(q) \) in the framework of \( \mathbf{r}_n \) as follows:

\[
A(q) = \int \left[ \sum_n \rho_n (\mathbf{r} - \mathbf{r}_n) \right] \exp(-i\mathbf{q} \cdot \mathbf{r} - i\mathbf{q} \cdot \mathbf{r}_n + i\mathbf{q} \cdot \mathbf{r}_n) \, d\mathbf{r}
\]

\[
= \sum_n \left[ \int \rho_n (\mathbf{r} - \mathbf{r}_n) \exp(-i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}_n)) \, d(\mathbf{r} - \mathbf{r}_n) \right] \exp(-i\mathbf{q} \cdot \mathbf{r}_n)
\]

\[
= \sum_n \int f_n(q) \exp(-i\mathbf{q} \cdot \mathbf{r}_n), \tag{2.4}
\]

where the index \( n \) runs over all atoms included in the sample and \( f_n(q) \) is the so-called atomic form factor for the \( n \)th atom [40,41], which is the Fourier transform of its electron density, as evidenced in equation (2.5),

\[
f_n(q) = \int \rho_n(\mathbf{r}) \exp(-i\mathbf{q} \cdot \mathbf{r}) \, d\mathbf{r}. \tag{2.5}
\]

Considering that the atoms can be approximated as spheres, the atomic form factor \( f_n(q) \) can be expressed as a function of the modulus of \( \mathbf{q}(= q) \), i.e. \( f_n(q) \). The scattered intensity can be therefore expressed as in the following equation:

\[
I(q) = \left| \sum_n f_n(q) \exp(-i\mathbf{q} \cdot \mathbf{r}_n) \right|^2
\]

\[
= \left[ \sum_n f_n(q) \exp(-i\mathbf{q} \cdot \mathbf{r}_n) \right] \left[ \sum_m f_m(q) \exp(i\mathbf{q} \cdot \mathbf{r}_m) \right]
\]

\[
= \sum_n \sum_m f_n(q) f_m(q) \exp(-i\mathbf{q} \cdot (\mathbf{r}_n - \mathbf{r}_m)). \tag{2.6}
\]

The described physical phenomena and related set of equations have a general value, and can be indistinctly applied to any kind of sample. In the case of crystalline materials (crystallography), the periodic long-range ordering arrangement of atoms inside the crystal lattice allows further elaboration of the general form in equation (2.6), leading for instance to Laue conditions [39,41]. In such a case, the elastic scattering process is commonly referred to as diffraction, and the scattered intensity \( I(q) \) is characterized by sharp, well-defined Bragg peaks appearing at discrete \( q \)-values.
\[ q = h \mathbf{a}^* + k \mathbf{b}^* + l \mathbf{c}^* \]

belonging to the reciprocal lattice. When the ordering level of the investigated sample is lowered (single molecules in the gas or liquid phase or amorphous materials), the scattering signals are diffused in the entire \( q \)-space and, due to random molecular orientation, the three-dimensional information is reduced to one dimension, and can be extracted from isotropic scattering patterns (vide infra). In a diffraction experiment from a crystalline sample, if the phases and amplitudes of \( hkl \) reflections have been obtained, we can directly reconstruct the three-dimensional electron density \( \rho(r) \) from the experimental dataset. Conversely, such a direct and univocal relation (\textit{diffraction pattern} \( \leftrightarrow \) \textit{three-dimensional structure}) is no longer valid for non-crystalline systems, due to a lowering in the information content. In this case, the data analysis strategy requires a conceptual inversion of the previous relation [43]. The relation changes into \textit{hypothetical three-dimensional structures} \( \leftrightarrow \) \textit{simulated scattering patterns}. The best fit of experimental one-dimensional scattering curves then provides the most plausible three-dimensional structure. These considerations emphasize the crucial role of theoretical modelling for the interpretation of scattering data from non-crystalline environments, even more importantly when the time-resolved case is considered.

(b) X-ray scattering from non-crystalline samples

In non-crystalline samples (gases, liquids and amorphous materials), where only short-range ordering is present, the probed volume is constituted by a statistical ensemble of sub-systems (molecules) randomly oriented. In this case, we are allowed to isotropically average equation (2.6) [40,41,43,44], thus obtaining a greatly simplified formula in which the scattered intensity is expressed as a function of one instead of three spatial dimensions. The resulting form is named the Debye equation [45], which is as follows:

\[
I(q) = \sum_n \sum_m f_n(q) f_m(q) \frac{\sin(q r_{nm})}{q r_{nm}},
\]

(2.7)

where \( r_{nm} = |r_n - r_m| \).

The Debye equation represents the key theoretical instrument in interpreting results from X-ray scattering experiments involving non-crystalline samples. However, the direct use of equation (2.7) is associated with some critical issues, in particular, passing from gas-phase to liquid-phase scattering. First, when dealing with many-atom systems (more than 500 atoms), calculation using the Debye equation is extremely resource consuming due to the extremely high number of possible combinations of \( n \) and \( m \) indexes; moreover, in liquid-phase systems, interatomic distances are continuously changing, making direct use of the Debye equation often inadequate.

For these reasons, it is useful to express the Debye formula in terms of RDFs \( g_{nm}(r) \) [46–48]. RDFs are defined in such a way that the probability of finding an \( m \)-type atom at distance \( r \) from an \( n \)-type atom is equal to \( 4\pi r^2 g_{nm}(r) \) (figure 3a shows a schematic representation of how RDFs are obtained). Using the formalism of RDFs, equation (2.7) can be reformulated as follows [41]:

\[
I(q) = \sum_n N_n^2 f_n^2(q) + \sum_{m} \sum_{n \neq m} \frac{N_n N_m}{V} f_n(q) f_m(q) \int_0^{\infty} g_{nm}(r) \frac{\sin(q r)}{q r} 4\pi r^2 \, dr,
\]

(2.8)

where the indexes \( n \) and \( m \) run over all the atom types included in the sample, \( N_n \) and \( N_m \) are the numbers of \( n \)-type and \( m \)-type atoms, respectively, and \( V \) is the volume of the sample probed by X-rays.

In the case of gas-phase scattering, the RDF \( g_{nm}(r) \) can be approximated to a Dirac delta function and, consequently, equation (2.8) reduces again to equation (2.7). Equation (2.8) highlights the possibility of obtaining a simulated \( I(q) \) curve directly using the \( g_{nm}(r) \) functions for the system of interest, to be used for comparison with the measured scattering data. Hence, this represents the theoretical basis for modelling and interpretation of static but also time-resolved X-ray scattering experiments, providing a direct connection between the acquired scattered intensity and structural features of the sample.
Figure 3. (a) Scheme of the radial distribution function (RDF) $g(r)$. The RDF is a measure to determine the correlation between particles within a system. Specifically, it is an average measure of the probability of finding a particle at a distance of $r$ from a given reference particle. The general algorithm involves the determination of the number of particles within $r$ and $r + dr$ (circular yellow shell in the figure) from the reference particle (represented in magenta). (b) Different contributions to the global scattering signal from a solution. (Online version in colour.)

(c) Static X-ray solution scattering

Hereinafter we will focus on the case of X-ray scattering from a liquid solution, i.e. a mixture of a minor component (solute) dissolved in a major component (solvent). X-rays are scattered by all the atoms included in the probed sample, both solute and solvent atoms. The global scattering signal from a solution can then be decomposed into three contributions \[26,49–52\], schematically indicated in figure 3b.

(i) Solute–solute terms, including scattering only from solute molecules, as in the gas-phase case. For these contributions, the indexes $n$ and $m$ of the related partial $g_{nm}(r)$ function account for the solute-only atoms. Generally, the distance between different solute molecules is big enough to neglect the signal derived from the interference between different solute units. Therefore, only the pairs belonging to a single molecule can be considered.

(ii) Solute–solvent (cage) terms, including contributions to scattering due to the cross interference between solute and solvent atoms, hence representing the structural arrangement of the solvent molecules around each solute unit. Corresponding partials $g_{nm}(r)$ have the index $n$, accounting for solute atoms, while the index $m$ accounts for solvent atoms.

(iii) Solvent–solvent terms, describing the scattering contribution from the bulk solvent, mainly influenced by the thermodynamic conditions. In this case, both the indexes $n$ and $m$ in partials $g_{nm}(r)$ run over solvent atoms.

In summary, the global scattered intensity can therefore be schematically expressed as in the following equation:

$$I(q) = I_{\text{solute}}(q) + I_{\text{cage}}(q) + I_{\text{solvent}}(q).$$

As electrons are responsible for the X-ray scattering signal, the order of magnitude of the $I_{\text{solvent}}(q)$ signal over the measured $I(q)$ can be estimated by calculating the ratio between the solute and solvent electrons and considering the solution concentration. If $n_e^{\text{solute}}$ and $n_e^{\text{solvent}}$ are the number of electrons of a single solute and solvent molecule, respectively, and if $x$ is the molar ratio between solute and solvent, then

$$\xi = \frac{\int I_{\text{solute}}(q) \, dq}{\int I(q) \, dq} \sim \frac{\int I_{\text{solute}}(q) \, dq}{\int I_{\text{solvent}}(q) \, dq} = \left( \frac{x n_e^{\text{solute}}}{n_e^{\text{solvent}}} \right)^2.$$
Figure 4. (a) Schematic representation of the experimental set-up for ultrafast XSS, on the model of the ID09b beamline of the ESRF. (b) Photographic views of the ID09b liquid-jet cell and FReLoN two-dimensional CCD detector [53], left-hand and right-hand panels, respectively. (c) Example of experimental data collected on 20 mM cis-[Ru(bpy)2(py)2]Cl2 in water. Left ordinate axis: superimposition of $I(q, \tau = 800 \text{ ns})$ and $I(q, \tau_0 = -1200 \text{ ns})$ curves (open violet circles and pink dots, respectively), both obtained by azimuthal averaging of a single CCD image. Right ordinate axis: difference signal $\Delta I(q, \tau = 800 \text{ ns}) = I(q, \tau = 800 \text{ ns}) - I(q, \tau_0 = -1200 \text{ ns})$, obtained using a single pair of laser-on–laser-off CCD images (light green curve), and after averaging 530 acquisitions (dark green curve). Parts of this figure are reproduced with permission from [54]; copyright ACS 2010. (Online version in colour.)

(d) Ultrafast X-ray solution scattering: experimental strategies

The three contributions discussed above for a static XSS experiment, equation (2.9), remain fundamental also in the case of time-resolved measurements. In such a case, a small portion of the sample is probed at time delay $\tau$ after laser excitation, generally inducing very small structural modifications.

A typical experimental set-up for ultrafast XSS is described in figure 4 in the model of the ID09b beamline [52,55–63] of the European Synchrotron Radiation Facility (ESRF) (ESRF website: http://www.esrf.eu/). Other beamlines dedicated to TR-XSS (for instance, beamline NW14A [64] (NW14 beamline @KEK website: http://pfwww.kek.jp/adachis/NW14/NW14.htm) of PF-AR at KEK (PF-AR@ KEK website: http://www-pfing.kek.jp/PF/index_html) and beamline 14-ID-B (14-ID-B beamline at APS website: http://cars9.uchicago.edu/biocars/pages/idb.shtml) at the Advanced Photon Source (APS) (APS website: http://www.aps.anl.gov/) employ analogue set-ups. An ultrafast pulsed laser system is required to excite the sample at the desired wavelength. The sample solution (0.1–100 mM) is continuously circulated within a liquid-jet apparatus. The synchrotron is employed to produce ultrafast X-ray probe pulses (60–150 ps, depending on the source operation mode), generally extracted from undulator insertion devices. In addition, a high-speed chopper, rotating at the same frequency of the laser, is employed to select a single X-ray pulse from the pulse train emitted by the synchrotron, to meet the readout time of charge-coupled
device (CCD) area detectors generally used to collect scattered X-rays. The two-dimensional images acquired by the CCD camera, after a series of corrections (pixel/optical fibres connection; fluorescent screen non-homogeneity; X-ray beam polarization; X-ray to visible photon conversion efficiency due to the \( \theta \)-dependence of the optical path through the fluorescent screen; X-ray extinction due to sample) are azimuthally averaged, resulting in one-dimensional \( I(q, \tau) \) curves. These curves are expressed as a function of the modulus of the wavevector \( q \) exchanged in the elastic scattering process, \( q = 4\pi \sin \theta / \lambda \), where \( \theta \) is the scattering angle and \( \lambda \) is the wavelength of the incident X-ray probe pulse, and of the selected pump–probe time delay \( \tau \).

A complete description of the experimental set-up details and of the strategies for data collection/reduction is beyond the aim of this work, and can be found elsewhere [43,55,65].

The effective photo-induced signal is enhanced by considering the difference between the X-ray scattering signal of the sample after (positive delays) and before (negative delay) laser irradiation. Therefore, differential scattered intensity, defined as \( \Delta I(q, \tau) = I(q, \tau) - I(q, \tau_0) \), is calculated.

A crucial point in time-resolved solution scattering is the smallness of the differential signal, when compared with the static scattered intensity \( I(q) \). Figure 4c shows, as an example, the case of a 20 mM solution of cis-[Ru(bpy)2(py)2]2+ in water, measured at the ID09b beamline of the ESRF [54]. On the left ordinate axis of the figure \( I(q, \tau = 800 \text{ ns}) \) and \( I(q, \tau_0 = -1200 \text{ ns}) \) curves obtained after azimuthal averaging of an individual pair of CCD images are superimposed (open violet circles and pink dots, respectively). The striking similarity between the static scattering signatures of the Ru solution before and after the laser excitation is evident: the two curves are apparently indistinguishable. However, when the differential scattered intensity \( \Delta I(q, \tau = 800 \text{ ns}) = I(q, \tau = 800 \text{ ns}) - I(q, \tau_0 = -1200 \text{ ns}) \) is calculated (figure 4c, right ordinate axis, light green curve), a quite noisy, but structured signal, with well-defined maxima and minima, is obtained. As can be noticed by comparing the values on the left and right axes, the ratio \( \Delta I(q, \tau)/I(q, \tau) \) is of the order of \( 10^{-3} \). Consequently, a single \( \Delta I(q, \tau) \) curve is affected by a very low signal-to-noise ratio, and huge statistics are required to obtain data of satisfactory quality. A noticeable improvement in data quality is observed after acquiring 530 CCD images for each time delay and averaging the corresponding \( \Delta I(q, \tau) \), as reported in figure 4c, dark green curve.

(e) Ultrafast X-ray solution scattering: theoretical modelling

The differential scattering signal acquired using the experimental approach described previously can be interpreted in straight analogy to the static case. Starting from equation (2.9), the global differential scattered intensity \( \Delta I(q, \tau) \) is given by the sum of three contributions, due to the changes in solute–solute, solute–solvent (cage) and purely-solvent terms. The time-dependent \( \Delta I(q, \tau) \) can therefore be expressed as in the following equation:

\[
\Delta I(q, \tau) = \Delta I(q, \tau)_{\text{solute}} + \Delta I(q, \tau)_{\text{cage}} + \Delta I(q, \tau)_{\text{solvent}}.
\]  

(2.11)

The major contribution to the \( \Delta I(q, \tau) \) signal is the solvent response to the heat release from the solute molecules excited by the laser pulse, \( \Delta I(q, \tau)_{\text{solvent}} \) in equation (2.11). This term is sensitive to the physical quantities determining the thermodynamic state of the bulk solvent as temperature, density and pressure, which are strongly influenced by the solute–solvent interplay and energetic transfer occurring during a photoreaction [43,65]. A careful modelling of the solvent–solvent contribution is therefore strictly required to isolate structural information on solute (or at least caged-solute) units, embedded in such a huge solvent-related background. After the ultrafast heat release from photo-excited solutes, a first stage of isochoric heating of the solvent can be identified: in this initial phase, the temperature and pressure rise without volume (and thus density) changes [51,52]. According to classical hydrodynamic theory [66], and using typical parameter values found in a time-resolved XSS experiment, this regime can be estimated to last up to approximately 10 ns from laser excitation. Subsequently, for time scales in the range 10–100 ns, the pressure relaxation occurs with the expansion of the solvent, up to a final thermodynamic equilibration point where solvent temperature and volume are slightly higher than the unperturbed laser-off values [67]. Under the hypothesis of local thermal equilibrium...
of the solvent, the solvent-only contribution $\Delta I(q, \tau)_{\text{solv}}$ can be expressed using only a pair of hydrodynamic variables. For example, selecting the temperature $T$ and the density $\rho$, we obtain the sum of differentials in equation (2.12), where $\frac{\partial I}{\partial T}$ and $\frac{\partial I}{\partial \rho}$ indicate, respectively, the solvent temperature and density variations from the moment of laser excitation ($\tau = 0$) to a desired time delay $t = \tau$,

$$\Delta I(q, \tau) = \left(\frac{\partial I}{\partial T}\right)_\rho \Delta T(\tau) + \left(\frac{\partial I}{\partial \rho}\right)_T \Delta \rho(\tau). \quad (2.12)$$

After the definition of the theoretical framework for modelling of solvent-related terms, the critical point shifts to the determination of the $(\partial I/\partial T)_\rho$ and $(\partial I/\partial \rho)_T$ differentials, which can be considered time-independent signatures of the specific thermodynamic behaviour for each kind of solvent. To complete this task, two major strategies have been applied. A first approach is the fully computational one, based on molecular dynamics (MD) simulations [50,67]. Solvent differentials can also be obtained by performing a separate solvent-heating experiment [51], thus bypassing the limitations of the purely computational approach (influence of the selected potential, difficulties in the modelling of the force field related to hydrogen bonds, finite size of the simulation box, etc.). The experimental procedure, first proposed by Cammarata et al. [51], consists of the vibrational excitation with near-IR pulses of pure solvent, subsequently probed by 100 ps X-ray pulses at selected time delays. Analysis of the time-resolved data allows one to extract the two key differentials. In particular, the isochoric term $(\partial I/\partial T)_\rho$ is mainly relevant at very short delays ($\tau \sim 100 ps$), while the $(\partial I/\partial \rho)_T$ differential becomes important at longer time scales ($\tau \sim 1 \mu s$). By substituting differentials from MD simulation with the experimentally determined ones, a noticeable improvement in the quality of the fit was found [51]. Under certain conditions, accurate modelling of the solvent contribution $\Delta I_{\text{solv}}(q)$ can also be achieved by performing the same data acquisitions, but with the photoactive sample replaced by a solution containing a phochemically-inert solute that is able to transfer a similar amount of heat to the solvent per laser pulse. The $\Delta I_{\text{solv}}(q)$ curve obtained in these ways has to be scaled to minimize the difference between $\Delta I(q)$ and $\Delta I_{\text{solv}}(q)$ in the region 1.5–2.9 Å$^{-1}$, where the signal is dominated by the thermal rearrangement effects of the bulk water structure. The scaled $\Delta I_{\text{solv}}(q)$ can thus be subtracted from the overall signal $\Delta I(q)$, to give the solute-related contribution to the differential scattered intensity $\Delta(\Delta I(q)) = \Delta I(q) - \Delta I_{\text{solv}}(q)$ [54,68].

Once all the contributions to the time-dependent differential scattered intensity are properly modelled, the state-of-the-art approach for data analysis consists of the ‘global-fitting analysis’ [31,58]. This method relies on the simultaneous fitting of TR-XSS data in $q$-space for all the delays investigated, instead of separately simulating the $\Delta I(q, \tau)$ curves for each $\tau$. Global-fitting parameters include the rate constants for all reaction pathways, the fraction of excited molecules, the branching ratios among excited molecules and, when needed, the geometrical parameters (bond lengths and angles) of all putative species involved in the photoreaction [65].

The global-fit analysis is performed directly in $q$-space, where the structural information is primarily contained. However, working in reciprocal space often excludes a straightforward and intuitive interpretation. For this reason, results are often presented in real space, after a sine-Fourier transform operation [43,54,69]. Indeed, a real-space TR-XSS signal represents the differential atom–atom pair distribution function during the course of the reaction [49,51,52,54,70,71]. Positive and negative peaks in real-space curves indicate, respectively, formation or cleaving of chemical bonds at the corresponding interatomic distances.

3. X-ray transient absorption: theoretical background and experimental strategies

The aim of this section is to provide the reader with a concise review of the basic physical principles on which the interpretation of XAS data is based. For a more detailed description of the theoretical background and experimental aspects of XAS, we refer to the extensive specialized literature (e.g. [72–78]).
Figure 5. (a) General behaviour of the X-ray absorption coefficient $\mu$ as a function of the incident X-ray energy $E$. (b) X-ray absorption edges nomenclature and representation of their relation with the atomic orbitals from which the electron is extracted. (c) Ru K-edge XAS spectrum for cis-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ in aqueous solution. The conventional division between the XANES and EXAFS region and the schematic models of multiple- and single-scattering processes, dominating, respectively, the XANES and EXAFS region, are indicated (colour code: absorber atom in magenta; neighbouring atoms that backscatter the photoelectron wave outgoing from the absorber in green). (Online version in colour.)

(a) X-ray absorption spectroscopy theoretical background

XAS measures the variations of the X-ray absorption coefficient $\mu$ as a function of the incident X-ray energy $E$. According to the Fermi golden rule [79,80], the XAS signal is proportional to the electron transition probability from the core state $|i>\rangle$ of energy $E_i$ to the unoccupied state $|f>\rangle$ of energy $E_f$, as expressed by the following equation, where the product $e \cdot r$ indicates the electronic transition dipole operator [81], $\rho_i$(occ) and $\rho_f$(unocc) are the densities of the initial occupied and final unoccupied states, respectively, and $\delta(E_f - E_i - E)$ is a Dirac delta function [78]:

$$\mu(E) \propto | <i| e \cdot r |f> \rangle|^2 \delta(E_f - E_i - E) \rho_i$(occ)$\rho_f$(unocc). \hspace{1cm} (3.1)$$

The behaviour of the $\mu(E)$ function is represented in figure 5a. A general decrease of the absorption with increasing incident energy can be noted, approximately following the law $\mu(E)/\rho \approx Z^4/AE^3$, where $\rho$ is the sample density, $Z$ is the atomic number and $A$ is the atomic mass. This equation holds for a sample containing a unique chemical species such as a metal foil, but can be easily generalized for any sample of known composition. In figure 5a the presence of the characteristic saw-tooth-like edges is evident. Their energy positions are a distinctive feature of each kind of absorbing atom. These absorption edges correspond to transitions where a core orbital electron is excited to (i) the free continuum (i.e. when the incident energy is above the ionization energy of the absorber atom) or (ii) unoccupied bond states lying just below the ionization energy. The nomenclature adopted for the edges recalls the atomic orbitals from which
the electron is extracted, as shown in figure 5b: K-edges are related to transitions from orbitals with the principal quantum number $n = 1(1s_1/2)$, L-edges refer to electrons from the $n = 2$ orbitals ($L_1$ to $2s_1/2$, $L_2$ to $2p_{1/2}$ and $L_3$ to $2p_{3/2}$ orbitals), and so on for the M, N, ... edges.

When the energy of the X-ray photon exceeds the ionization limit (case (i) mentioned above), the excited electron (generally named ‘photoelectron’) has a kinetic energy $E_K$ given by $E_K = h\nu - E_B$, where $E_B$ indicates the electron binding energy that is typical of the absorption edge (K, L$_1$, L$_2$ or L$_3$) of the selected atomic species [82]. This makes extended X-ray absorption fine structure (EXAFS) an atomically selective technique that provides information on the selected atom only [83]. In the studies of the local environment of highly diluted species [84–86], this is a great advantage of EXAFS with respect to scattering techniques, where all atoms present in the sample contribute to the signal. In the particular case of transition metal complexes in solution relevant in this review, comparing EXAFS with XSS, it is evident that the EXAFS signal contains only the solute and the cage contributions, while the solvent contribution (that dominates the XSS signal) is totally absent; see equations (2.9) and (2.11). Once ejected, the photoelectron propagates through the sample as a spherical wave diffusing from the absorber atom, with a wavevector of modulus $k$ defined by the following equation:

$$k = \frac{2\pi}{\hbar} \sqrt{2m_e E_K}. \quad (3.2)$$

A close zoom on the energy region in proximity of an absorption edge shows a well-defined fine structure. In particular, only when the absorber is surrounded by neighbouring atoms (molecules or crystals) does a structure of oscillatory nature modulate the smooth $\mu(E)$ profile at energies above the edge. An example is provided for cis-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ (aqueous solution) in figure 5c, where the energy range around the Ru K-edge—highlighted in magenta in part (b) of the same figure—is expanded to appreciate the edge fine structure and the associated oscillations. Such modulation in the absorption coefficient is derived from the interference between the outgoing photoelectron wave diffusing from the absorber and the wavefronts backscattered by the neighbouring atoms [87,88]. In a typical XAS experiment, the energy range around the edge probed is conventionally divided into two different regions (figure 5c):

(i) X-ray absorption near edge structure (XANES) region: portions of the XAS spectrum just below and above the edge energy and

(ii) extended X-ray absorption fine structure (EXAFS) region: portions at higher energies with respect to the edge (from tens to hundreds of eVs), characterized by the oscillatory modulation in the absorption coefficient.

Next, we will briefly discuss the main information that can be extracted from the analysis of each of the two regions listed above.

(b) The X-ray absorption near edge structure region

The XANES region can be further divided into three main sub-intervals: we can distinguish the pre-edge region, the absorption edge and the post-edge region, up to 30–50 eV after the edge jump. The investigation of these three portions of the XANES spectrum and the interpretation of the different physical phenomena governing their characteristic features provides plenty of information, both of electronic and structural nature [77,82,89–97].

The pre-edge region can include well-defined components, related to electronic transitions from the core level to empty bound states [98], as, for example, the unoccupied states of the narrow d-band lying just above the Fermi energy in transition metals. The features of the pre-edge peaks are directly influenced by the density of states and the occupancy of states; therefore, their investigation is extremely helpful in unravelling the electronic structure of molecules [77,82,98,99]. Moreover, the intensity of pre-edge peaks is governed by the selection rules for dipolar transitions, which can be relaxed depending on the local symmetry around the absorber.
atom [100]. Pre-edge features related to transitions that are formally forbidden in the purely dipolar case can, however, appear in the XANES spectrum, hence providing information about the geometrical coordination environment of the absorber.

The energy position of the absorption edge is sensitive to the oxidation state of the absorber [82, 101,102] due to the charge-shielding effect on the ionization energy (practically, a higher oxidation number corresponds to an edge shift towards higher energies). In addition, the edge location is influenced by the coordination geometry, which ultimately is determined by the energy position of molecular orbitals [25].

The edge and post-edge regions are particularly sensitive to the geometrical arrangement of the neighbouring atoms in the restricted local cluster around the absorber. This makes XANES a very powerful instrument for direct structural characterization in a wide range of systems, including semiconductors [83,103], superconductors [104], oxides [105–109], catalysts [82,102,110–117], solutions [118], surfaces and interfaces [119–121], and biological [122–126], geological [127–130] and hybrid organic–inorganic materials [113,131–133]. The relation between geometrical features and XANES response mainly depends on the multiple-scattering processes (figure 5c) of the excited photoelectron after the ionization threshold, which dominate with respect to the single-scattering events due to the lowered photoelectron energy. Moreover, the first 10 eV after the ionization limit are, in many cases, influenced also by other kinds of physical interactions, directly dependent on the properties of the investigated sample (so-called ‘shape resonances’ in molecules, core excitons in crystals, unoccupied local electronic states in metals and insulators [28]).

(c) The extended X-ray absorption fine structure region

The EXAFS region of the spectrum is located at higher energies and is characterized by the modulation of the absorption coefficient $\mu(E)$. Such a feature is caused by the interference between the X-ray waves diffused by the absorber atom and those backscattered by its neighbours. Hence, EXAFS oscillations can be related via Fourier transform to a specific spatial arrangement of the atoms in the local environment of the absorber, bridging the energy space to the real distances $R$-space. This crucial point is the basis of the EXAFS analysis procedure developed after the milestone works of Sayers, Lytle and Stern [87,88,134].

The higher photoelectron kinetic energy in the EXAFS region implies that the phenomenon is no longer dominated by the full multiple-scattering regime, which instead dominates in the XANES region [134]; consequently, data analysis can be performed using the simpler Fourier transform operation [82,87].

The EXAFS signal $\chi(E)$ is generally expressed as the oscillatory part of the $\mu(E)$ function, normalized to the edge jump, i.e. $\chi(E) = [\mu(E) - \mu_0(E)]/\Delta\mu_0(E)$, where $\mu_0(E)$ is the atomic-like background absorption and $\Delta\mu_0(E)$ is the normalization factor. Above the absorption edge, the energy $E$ can be substituted with the photoelectron wavevector $k$ using equation (3.2), therefore obtaining the EXAFS function $\chi(k)$. The relation between the modulation of the $\chi(k)$ signal and the structural parameters is provided by the EXAFS formula that, in the single-scattering approximation, is reported in the following equation:

$$\chi(k) = S_0^2 \sum_i N_i F_i(k) e^{-2\sigma_i^2 k^2} e^{-(2\pi i / \lambda(k))} \sin\left[2kr_i + 2\delta_i(k) + \theta_i(k)\right] / k^2 r_i^2,$$

where $S_0^2$ is the overall amplitude reduction factor, the index $i$ runs over all the different shells of neighbouring atoms around the absorber, $F_i(k)$ is the backscattering amplitude as a function of $k$ for each shell, $N_i$ is the coordination number (number of equivalent scatterers) and $\sigma_i^2$ is the Debye–Waller factor accounting for thermal and static disorder. The parameter $r_i$ indicates the interatomic distance of the $i$th shell from the central absorber. The phase shift of the photoelectron is distinguished in two contributions, related to the absorber ($2\delta_i$) and to the scatterer ($\theta_i$). The term $\lambda(k)$ is the energy-dependent photoelectron mean free path, typically a few Å, determining the local nature of the technique that can investigate only up to $\approx 5$–8 Å around the photo-excited
atom. This apparent limitation of EXAFS is conversely a big advantage in the investigation of disordered materials such as glasses or liquids, as the long-range order is not required [82].

(d) Ultrafast X-ray absorption spectroscopy: challenges and possibilities

Ultrafast laser pump X-ray probe XAS experiments have been proposed since the end of the 1990s [135–138]. Initially, the time resolution of these studies was limited to the ms–ns range [139–142], except for one groundbreaking case [143]. Theoretical and experimental critical issues had to be considered to extend the feasibility of time-resolved XAS characterization to the sub-ns time domain.

Theoretically, efforts were devoted to the study of time-dependent XAS signals, considering the wavepacket dynamics in the photo-excited state, the ‘real-time’ coherent atomic motions and the finite duration of the X-ray probe pulse [135]. The coherent dynamics is limited to extremely short time scales. The whole X-ray-matter interaction process, including photoelectron ejection, backscattering and interference, is mostly completed after ca 1 fs from excitation [144]. This ensures that the XAS technique catches snapshots of ‘frozen’ atoms, even during a chemical reaction.

From the experimental point of view, in particular, for the investigation of ultrafast dynamics in solution, the issues that had to be overcome are hereafter listed and briefly discussed.

(i) A continuously tunable monochromatic X-ray source that is able to provide ultrashort pulses is required.

(ii) The absorption cross sections for the optical pump and the X-ray probe pulse differ by two to three orders of magnitude. Typical values for the extinction coefficients of molecules in the UV–vis spectral region are in the range $10^3$–$10^7 \text{ M}^{-1} \text{ cm}^{-1}$, while in the case of X-rays, these values are lowered by a factor of $10^2$ or even $10^3$; see figure 5a. Operatively, if the solution sample thickness is optimized to maximize laser excitation, the majority of the X-ray photons are absorbed by the solvent instead of the element of interest. Conversely, if the experimental conditions are tuned to optimize the X-ray absorption by atoms of the element selected, the resulting sample concentration is generally too high to allow the laser pulse to photo-excite a significant fraction of solute molecules. In most cases, a diluted solution optimized for photo-excitation is chosen, and the fluorescence detection scheme for XAS spectra acquisition is preferred to the transmission mode [145–147]. A generally adopted rule of thumb consists of maintaining the number of solute units and the number of photons of the pump laser pulse at the same order of magnitude (ca $10^{13}–10^{15}$ photons/pulse for commercial fs laser systems) to maximize the sample excitation [148].

(iii) The maximum intensity achievable for ultrashort X-ray pulses is not very high. Typically, values of $10^6$ photons/pulse are obtained, even using third-generation synchrotron facilities. Moreover, an extremely sensitive detection system is required since photo-induced structural modifications are generally of limited entity and the pump pulse excites all the solute molecules in the volume probed by X-rays.

A detailed analysis of these difficulties, and of the specific strategies consequently developed to optimize ultrafast XAS experiments can be found in specialized literature reviews [25,28].

However, the feasibility of time-resolved XAS with sub-ns resolution has nowadays been demonstrated [137], and several dedicated beamlines are operative worldwide, e.g. 11-ID-D beamline (11-ID-D beamline @ APS website: http://www.aps.anl.gov/Beamlines/Directory/showbeamline.php?beamline_id=17) at the APS (Illinois, USA), the MicroXAS beamline (Micro-XAS beamline @ SLS website: http://www.psi.ch/sls/microxas/) at the Swiss Light Source (Switzerland), and the 6.0.1 beamline (6.0.1 beamline @ ALS website http://www-als.lbl.gov/index.php/about-the-als/als-in-the-news/106-601.html) at the Advanced Light Source (California, USA).
(e) Ultrafast X-ray absorption spectroscopy characterization of photo-excited metal complexes in solution: theoretical models and strategies for data interpretation

The XAS spectrum of a laser-excited metal complex in solution is a combination of the ground state (GS) and of the different possible ES spectra, as the pump pulse is not able to excite all the molecular units in the probed volume. A bottleneck before obtaining detailed dynamical structural information from time-resolved XAS is the discrimination of the different species involved, each characterized by a different coordination geometry around the X-ray absorber atom. A crucial aspect is the extraction of the ES spectrum (or spectra in the case of multiple simultaneously populated ESs). For this purpose [25], the global XAS signal from a laser-pumped sample can be modelled as in the following equation:

$$\mu(E, t) = \left[ 1 - \sum_i f_{ES}(t) \right] \mu_{GS}(E) + \sum_i f_{ES}(t) \mu_{ES}(E, t),$$  

(3.4)

where $\mu(E, t)$ is the total time-dependent X-ray absorption, as a function of the probe X-ray photon energy $E$, $f_{ES}$ is the fraction of the $i$th ES (at time $t$), and $\mu_{GS}(E)$ and $\mu_{ES}(E, t)$ are the XAS spectra of the GS and of the $i$th ES, respectively. A high-quality $\mu_{GS}(E)$ spectrum can be separately collected in a standard EXAFS experiment, so that it is a known function in the pump–probe EXAFS experiment.

The coherent dynamics of the excited system is lost after a few fs from laser excitation, and for time resolutions in the ps time domain, only thermally equilibrated ES structures can be probed. In such conditions, each of the ES XAS spectra are no longer time dependent, and it is possible to substitute the term $\mu_{ES}(E, t)$ in equation (3.4) with the static contribution $\mu_{ES}(E)$. In the simple case of a two-level system (the GS and a single ES), we can ideally set the time delay in order to probe the ES structure at its maximum concentration (nominally occurring at $\tau = 0$), thus obtaining the following equation:

$$\mu(E, \tau = 0) = [1 - f_{ES}(0)] \mu_{GS}(E) + f_{ES}(0) \mu_{ES}(E).$$  

(3.5)

Equation (3.5) contains two unknown parameters, $f_{ES}(0)$ and $\mu_{ES}(E)$. Additional information on at least one of these quantities is required to obtain a unique solution for the equation. The ES fraction at optimal ES concentration $f_{ES}(0)$ can be estimated by performing a separate laser pump–laser probe experiment, conducted in identical conditions (e.g. sample concentration and photo-excitation features) with respect to the time-resolved XAS study. Moreover, in some cases when additional information on the ES geometry is available, the $\mu_{ES}(E)$ contribution can be isolated, especially from the XANES portion of the XAS spectrum [148,149]. Once the ES signal is extracted, several codes can be employed to perform a combined fitting of the GS and ES structures in both the XANES [77,150–155] and EXAFS [77,156] regions.

Unfortunately, this approach can be employed only in a limited selection of cases. Often, during the photoreaction, several species coexist (ESs and eventually photoproducts) and even in simpler two-level systems, it is quite difficult to obtain a reliable estimate for the ES fractional population due to overlapping spectral features [157].

A valid alternative for the analysis of ultrafast XAS data in the EXAFS region has been recently developed by Chergui and co-workers [157–159]. Their approach bypasses the critical step of ES spectrum reconstruction, being based on the fitting of the difference spectrum $\Delta \mu(E, \tau) = \mu(E, \tau) - \mu_{GS}(E)$, directly in the energy/momentum space. The refinement is obtained by minimization of the square residual function between a large series of simulated differential EXAFS spectra and the experimental difference data. Operatively, EXAFS signals for a series of candidate ES geometries, characterized by a specific set of parameter values (bond lengths, Debye–Waller parameters $\sigma^2$, edge energy shift $\Delta E$), are simulated. Subsequently, the best-fit curve obtained from a standard EXAFS analysis of the GS EXAFS signal is subtracted from each calculated ES spectrum. The resulting simulated differential spectra are compared with the experimental differential signal, using a statistical figure to quantify the goodness of fit. This
method provides a superior accuracy for the derived structural parameters when compared to conventional EXAFS fitting methods, where structural modifications are extracted from the Fourier transform of the reconstructed ES EXAFS signal [160]. Using this approach, the influence of possible systematic errors in the calculations is drastically reduced [97].

Benfatto et al. proposed a similar strategy for the fitting of the difference spectra also in the XANES region [97]. They extended the capabilities of the previously developed fitting procedure MXAN [161] (based on a full multiple-scattering analysis [151]) to deal directly with differential XANES data. The method was successfully tested for the analysis of ps L3-edge XANES of [Ru(bpy)3]2+ in water solution, excited by a 400 nm ultrashort laser pulse [148,162].

4. Applications

In the previous sections, two different physical processes relying on the interaction of an X-ray pulse with the probed sample have been described, i.e. the elastic scattering and the absorption of the incident radiation. Both these phenomena are highly informative. They offer the unique advantage of a direct monitoring of the structural dynamics when integrated with ultrafast laser excitation in a pump–probe scheme. In this section, our aim is to provide a brief overview of the most exciting results achieved in the last few years using TR-XSS and TR-XAS, emphasizing the potential of these novel approaches in the elucidation of molecular structural dynamics in solution, where much relevant chemistry occurs, and where the complex solute–solvent interplay heavily influences the reaction pathway [65]. In particular, we will review in detail selected applications involving the solution photochemistry of transition metal complexes.

(a) X-ray scattering and X-ray absorption: global and local views on photoreactions

The signal detected from an X-ray scattering experiment unavoidably arises from all atom–atom pairs in the probed volume. In §2, we have carefully discussed the theoretical implications in the specific case of a solution, introducing the distinction between solute-only, cage and solvent-only contributions to the scattering signal; see equations (2.9) and (2.11). At reasonable solute concentration values, the signal is dominated by the solvent–solvent terms, thus making static X-ray scattering techniques unfavourable for investigating the structure of a diluted solute due to their limited sensitivity. In principle, this is also true in time-resolved experiments. The photo-excited solute relaxes, transferring the energy absorbed from the laser pump pulse to the solvent, which impulsively modifies its thermodynamic state (temperature, pressure and density). As a consequence, the differential scattering intensity is also dominated by the strong time-dependent background related to solvent-only thermodynamic response to laser excitation [43,51]. Nevertheless, such limitations can currently be elegantly overcome by proper analysis and interpretation of the solvent-related contributions. Indeed, X-ray scattering data treatment can lead to full comprehension of the solvent’s role in photochemical processes, an intriguing subject scarcely explored so far for metal complexes and other systems.

On the other hand, XAS spectroscopy provides structural information limited to the local environment of the X-ray absorbing atom (e.g. the metal ion), due to the shortness of the photoelectron free mean path; see in §3 the \( \exp(-2r_i/\lambda) \) factor in equation (3.3). The XAS signal is therefore intrinsically local, being limited within a spherical shell of 5–10 Å radius centred on the absorber. Thus, XAS provides a much higher sensitivity in comparison with X-ray scattering to elucidate the structure of a solute molecule, and, in the time-resolved case, to monitor its photo-induced modifications. To study ultrafast photochemical reactions of transition metal complexes in solution, the incident X-ray photon energy is tuned to one of the metal centre absorption edges. Combined analysis of the XANES and EXAFS region can provide local and highly selective information on the electronic and structural features of transition metal complexes, as well as on their temporal evolution.

In summary, ultrafast XSS provides a global and comprehensive view on the photoreaction structural dynamics including solvent rearrangements. The price to pay to have access to such
unique information is lost in sensitivity and an additional effort in data analysis. In contrast, TR-XAS offers local and element-selective evidence for structural differences in the first coordination shells around the absorbing atom, whilst missing what happens at larger distances. In particular, solvent cage rearrangement around photo-excited solute molecules is difficultly revealed, while the modifications in solvent bulk structure are completely silent.

The two ultrafast X-ray-based techniques are therefore highly complementary, and their integrated use can ensure a comprehensive understanding of the fascinating and, under several aspects, still elusive solution photochemistry of metal complexes.

(b) Ultrafast X-ray solution scattering applications: a brief overview

TR-XSS\(^1\) is able to capture, in one radial dimension, all the transient structures present in the laser-irradiated volume by collecting X-ray scattering patterns as a function of time delay. Data analysis of such patterns can then reveal the structural evolution of different reaction pathways, limited only by the signal-to-noise ratio of the difference signal between excited and non-excited states. In the last decade, TR-XSS has been successfully employed to monitor light-driven solution-phase structural rearrangements for a variety of systems, from small elementary molecules to proteins and macromolecules of biological relevance [43,65,69].

Examples of TR-XSS studies on the photochemistry of small fundamental molecules include systems as CHI\(_3\) [62], CBr\(_4\) [61], HgI\(_2\) [59], HgBr\(_2\) [163] and I\(_2\) and Br\(_2\) [49,52,164]. In all these cases, the technique revealed global and major reaction pathways and elucidated transient structures of intermediates for the photodissociation reaction.

Furthermore, TR-XSS was also applied in the investigation of the iodine elimination reaction in haloalkanes, disclosing also the solvent polarity role on the intermediates’ structure and their kinetics [58,63,165,166].

The variety of systems analysed using TR-XSS also includes the study of structural and thermal dynamics of gold nanoparticles suspended in water, after excitation with fs laser pulses [167–170]. Very recently, protein-coated gold nanoparticles were investigated by ultrafast X-ray scattering in a water suspension [171] to clarify laser-mediated effects on biomolecules under the conditions occurring in photothermal laser therapy with nanoparticles as photosensitizers.

Another very challenging but exciting field of application for TR-XSS is protein structural dynamics in solution. Notwithstanding difficulties related to sample preparation and data acquisition and analysis, TR-XSS has been successfully applied to monitor conformational changes in proteins, even with ns [172–174] and ps [175] time resolution. In the case of large biomolecules such as proteins, the structural information is contained both in the small-angle (SAXS) and in the wide-angle (WAXS) ranges [176–181]. Owing to the inverse relationship between scattering angle and interatomic distance, information on the global protein features (size, shape) can be extracted from analysis of the SAXS region of the scattering curve, while the WAXS region is particularly sensitive to tertiary and quaternary structure [69], and therefore to the folding of helices and sheets.

Using this combined TR-SAXS/WAXS method, the laser-induced conformational modifications in the tertiary and quaternary structure of human haemoglobin [172] and of the wild-type homodimeric haemoglobin from the Scapharca inaequivalvis clam [182] were elucidated with 100 ps time resolution. The myoglobin tertiary structure relaxation in response to the optically induced CO dissociation [172,183] and refolding of cytochrome c [172] were also investigated. Using a combination of double electron–electron resonance spectroscopy, NMR and TR-SAXS/WAXS, Ramachandran et al. first succeeded in directly monitoring the structural evolution of the transient signalling state of the photoactive yellow protein, considered a prototype photoreceptor [184]. These results were lately complemented by a detailed TR-SAXS/WAXS.

\(^1\)The technique has been referred in the literature using several different acronyms. In analogy with the term ‘crystallography’ but emphasizing the peculiar application to liquid-phase systems, it is often named time-resolved X-ray liquidography (TRXL). In other studies, the definitions time-resolved wide/small angle X-ray scattering (TR-WAXS/TR-SAXS) are used, depending on the angular range from which the structural information is extracted.
investigation of the structural changes occurring during the photocycle in a wide time range from 3.16 µs to 300 ms [185]. Finally, several TR-WAXS studies allowed one to visualize in real time the helical motions associated with proton pumping in bacteriorhodopsin [174] and proteorhodopsin [174, 186], clarifying the reaction kinetics along the photocycle.

Ultrasound XSS was also widely employed in the investigation of transition metal complex photoreactions in solution. Some of the most exciting applications are discussed in detail below.

(c) The solution-phase photochemistry of the transition metal photocatalyst Ru₃(CO)₁₂

TR-XSS investigation of the photo-induced rearrangements in the Ru₃(CO)₁₂ by Kong et al. [60, 187] demonstrates well the potential of a wise combination of ultrafast techniques, such as transient IR spectroscopy and TR-XSS. In addition, this study has served as a test bed to verify the robustness of the algorithms developed for TR-XSS data analysis, which is one of the most complicated cases investigated with such a method (as much as 16 different possible intermediates have been tested to reproduce the experimental data).

The Ru₃(CO)₁₂ triangular cluster is a paradigm system in the study of the photochemistry of transition metal carbonyls. Furthermore, this derivative acts as a photocatalyst in photo-activated synthesis, inducing the breaking of selective bonds depending on the excitation wavelength [188, 189]. Owing to the high practical and fundamental interest in the metal–metal bond cleavage mechanism, the Ru₃(CO)₁₂ metal cluster has been widely investigated, both in solution and in solid matrices, using various spectroscopic methods [189–197].

A recent transient IR study was performed on Ru₃(CO)₁₂ in cyclohexane solution upon both visible (400 nm) and UV (266 nm) excitation [197]. The results revealed the presence of two reaction intermediates. For the metal–metal bond breaking channel, the intermediate Ru₃(CO)₁₁(μ-CO) (I₁ in figure 6a) was isolated, while for the CO dissociation channel, the intermediate Ru₃(CO)₁₀(μ-CO) (I₂ in figure 6a) was detected. The main limit of this spectroscopic approach is the possibility of missing intermediate species containing only linear carbonyls (which are buried under the GS signals) and the poor structural sensitivity. TR-XSS is therefore a perfect complement for ultrafast IR characterization since it contains the scattering signal
contributions from all the reaction pathways (in proportion to their population and scattering function) and is highly sensitive to intermediate geometries [43,49,58,59,61–63,65,70,198–200].

Kong et al. first applied TR-XSS to the Ru$_3$(CO)$_{12}$ cluster in cyclohexane (3 mM solution, $\xi = 4.1 \times 10^{-6}$) upon visible light excitation at 390 nm, collecting scattering data at time delays ranging from 42 ps to 300 ns (figure 6b, black curves) [60]. The fit of TR-XSS data using only intermediates $I_1$ and $I_2$ previously isolated by IR characterization was unsatisfactory. This discrepancy highlighted the presence of at least a third transient species $I_3$ involved in the photoprocess, likely missed by transient IR measurements for the absence of bridging carboxyls. A noticeable effort was invested in the theoretical modelling by including: (i) simulation of the solutes-only contribution obtained from the difference between the Debye scattering curves of density functional theory (DFT)-optimized geometries of several putative intermediates and the parent molecule; (ii) simulation of the cage contribution for each putative transient species via MD; and (iii) deduction of the bulk-solvent response from separated impulsive heating experiments on the pure solvent excited by near-infrared laser pulses [51]. A very good level was reached in the simulation of the experimental data, as visible from best-fit theoretical $q\Delta I(q)$ curves reported for each delay in figure 6b. The full analysis demonstrated that the missing intermediate $I_3$, dominating the scattering signal at higher delays, is an isomer of the Ru$_3$(CO)$_{10}$ species characterized by an Ru$_3$ cluster with linear carboxyls only, and a lifetime of the order of tens of ns (see figure 6a for the $I_3$ structure).

The global-fit analysis also provided detailed insights into the reaction kinetics. Figure 6c shows the time-dependent changes in the concentration of the intermediate species identified after photo-excitation of Ru$_3$(CO)$_{12}$ with 260 nm and 390 nm light. In the case of visible light excitation at 390 nm, all the three intermediates were observed immediately after the reaction initiation, and all the transient species involved are found to finally evolve towards the reconstitution of the Ru$_3$(CO)$_{12}$ parent cluster with different lifetimes. Changes in the reaction kinetics depending on the excitation wavelength were further investigated by Kong et al. in later work [187]. The TR-XSS experiment discussed so far was repeated using an excitation wavelength of 260 nm. Upon UV light excitation, only the intermediates $I_1$ for the metal–metal cleavage channel and $I_3$ for the CO dissociation channel were detected at the onset of the photoreaction ($\tau = 100$ ps). Evidence for the formation of the Ru$_3$(CO)$_{10}$(μ-CO) species ($I_2$) was found only at later delays, suggesting a different pathway. Owing to differences in the available absorption bands, the Ru$_3$(CO)$_{10}$(μ-CO) intermediate is generated by bimolecular recombination of Ru$_3$(CO)$_{10}$ with a free CO, in ca 50 ns from excitation.

(d) The binuclear complexes [Pt$_2$(P$_2$O$_5$H$_2$)$_4$]$^{4-}$ and [Ir$_2$(dimen)$_4$]$^{2+}$

TR-XSS was successfully employed to elucidate photogenerated ES structure in two structurally related dinuclear metal complexes, namely tetraakis-μ-pyrophosphidoclaplatinate ([Pt$_2$(P$_2$O$_5$H$_2$)$_4$]$^{4-}$, Pt-POP) [199] and [Ir$_2$(dimen)$_4$]$^{2+}$, where (dimen) = 1,8-diisocyano-p-menthane [68]. These dimeric systems were selected primarily for their very interesting photochemical properties, but also due to the high scattering power ensured by the metal–metal atom pairs [201–203]. Both the studies highlighted substantial differences between the ES structural features found in solution and those obtained from previous solid-state characterization. This evidence emphasizes the peculiarity of the solution-phase photochemistry and consequently the importance of developing specific ultrafast characterization techniques and related analysis protocols.

Pt-POP is a square-planar molecule with $D_{4h}$-symmetry (figure 7a, left panel) that undergoes pronounced contraction along the metal–metal bond axis upon excitation of the 5dσ* → 6σ electronic transition [201]. Previous reports highlighted a $3\tilde{A}_{2u}$-symmetry lowest-lying triplet state [204,205], with a measured lifetime of 9.8 μs in deoxygenated water [206–208] and a quantum yield of approximately 100% [208]. The geometry of such a long-lived triplet state was thoroughly investigated in the crystal phase using both ultrafast [209–211] and stationary-state X-ray methods [212,213]. The crucial structural parameter is the contraction of the Pt–Pt bond distance, which
Figure 7. (a) The Pt-POP case. Left-hand panel: GS structure of the Pt-POP bimetallic complex (colour code: Pt blue, P yellow, O red); middle panel, from top to bottom: total difference signal at 100 ps (blue) and 1 µs (red) after optical excitation of 12 mM K₄Pt-POP in water; bulk-solvent difference-signal response as modelled for the two time delays; caged-solute contribution, obtained by subtracting the bulk-solvent response from the total difference signal; right-hand panel, experimental and best-fit solute-only differential scattering signals at the two investigated time delays. (b) The [Ir₂(dimen)₄]²⁺ case. Left-hand panel: GS structure of [Ir₂(dimen)₄]²⁺ (colour code: Ir purple, C grey, N blue). Middle panel: data (black points) and best-fit models (red lines) for time delays ranging from 250 ps to 300 ns after excitation. Right-hand panel, from top to bottom: magnification of the 30 ns delay experimental and simulated curves; contribution to best-fit simulation from structural changes in the solute (magenta), distinguishing signals related to the structural changes in the long (full) and short (dashed) isomers; bulk-solvent thermodynamic response (blue), partitioned into contributions due to expansion (full line) and heating (dashed line). Reproduced with permission from [199] (copyright ACS, 2009) and [68] (copyright ACS, 2011). (Online version in colour.)

was found to vary in the range 0.23–0.28 Å for crystalline samples. Christensen et al. provided a detailed characterization of the ES bond distances in the Pt-POP ³A₂u ES in water solution (12 mm, ξ = 9.4 × 10⁻⁵), from analysis of TR-XXS data collected at 100 ps and 1 µs after laser excitation at 267 nm [199]. The total difference signals (see figure 7a, middle panel) were analysed by applying a novel approach. The global-fitting procedure included solvent differentials determined using the so-called near-infrared method [51], with the values of temperature and density variations optimized within the fit. Special attention was devoted to structural modelling for simulation of the solute contribution. The GS structure was fixed after taking into account several geometries from X-ray diffraction (XRD) studies and geometries optimized using different DFT-based methods. For the ES structure, ca 1000 hypothetical geometries were considered by systematic variation of two key bond distances from GS values, i.e. the Pt–Pt bond length and the distance between the P planes. In addition, the excitation ratio (fraction of Pt-POP molecules in the ES when probed by X-ray) was optimized. The best fit was reached in correspondence to a 0.24 Å contraction of the Pt–Pt bond distance (i.e. 8% of the GS value), while the distance between P planes was found to be almost unperturbed, thus implying a slight lengthening of the Pt–P bond in the ³A₂u ES. Interestingly, the Pt–Pt bond contraction found by TR-XXS is less severe when compared to the 0.28 Å value obtained using ultrafast photocystallography [211,212]. It is noteworthy that the same system was further studied in a Pt L₃-edge TR-XAS experiment. Van der Veen et al. analysed the transient EXAFS spectrum in energy space directly, according to the method [158] mentioned in §3. A 0.31 Å contraction of Pt–Pt bonds was found, whereas a slight lengthening of 0.010 Å was observed for Pt–P bond distances with respect to GS values, in good agreement with theoretical calculations [214].
TR-XSS provided unique insights also on the GS and ES structure of the ligand-bridged bimetallic complex \([\text{Ir}_2(\text{dimen})_4]^{2+}\) in acetonitrile (6 mm solution, \(\xi = 6.6 \times 10^{-5}\)) [68], the structure of which is shown in figure 7b, left-hand panel. The trend expected for structural modifications in photo-excited \([\text{Ir}_2(\text{dimen})_4]^{2+}\) is the same as discussed above for the Pt-POP complex: light-induced population of a bonding orbital localized between the metal centres induces a pronounced contraction of the metal–metal bond distance [215]. In particular, Hardlup et al. extracted a triplet ES Ir–Ir distance of 2.90 Å. In the \([\text{Ir}_2(\text{dimen})_4]^{2+}\) case, the best agreement with scattering data was obtained by including in the global-fit model two GS structural isomers, differing in separation of metal centres (3.6 Å and 4.3 Å, respectively, see also fit contributions reported in figure 7b, right-hand panel) with equivalent population of 50% each. Such evidence confirmed and complemented recent spectroscopic results [216]. As in the Pt-POP case, a significant difference in the entity of metal–metal bond contraction has been highlighted, comparing results from solution and crystal phase characterization. For instance, the dramatic shortening of 1.4 Å with respect to the long-distance GS isomer is greater than the values found via steady-state XRD studies on the analogue Rh-containing compound \([\text{Rh}_2(\text{dimen})_4]^{2+}\) [217]. The authors explained such discrepancy with the absence of crystal packing forces, leading to an intensification of secondary deformation mechanisms already present in the crystal case.

A close inspection of the experimental data (and related simulations) reported in figure 7a (middle panel) and 7b (right-hand panel) deserves further comments. Commonly used solvents are molecules containing low-Z atoms such as C, O, N and H. For these atoms, the X-ray atomic scattering factors are functions that go rapidly to zero at high \(q\) values [218,219]. Conversely, high-Z atoms such as Pt (\(Z = 78\)) or Ir (\(Z = 77\)) are able to contribute to the overall scattering up to much higher \(q\) values. This is the reason why the much more abundant solvent molecules dominate the experimental \(q\Delta l(q)\) data up to about \(q \sim 4\ \text{Å}^{-1}\), while, for \(q > 4\ \text{Å}^{-1}\), the solute and cage contributions are predominant. In principle, the simplest way of treating the solvent contribution would be to analyse the high-\(q\) part of the data only. However, for the time being, this apparently simple solution is not feasible since, for \(q > 7\ \text{Å}^{-1}\), the experimental \(q\Delta l(q)\) data are dominated by noise and the interval \(4\ \text{Å}^{-1} < q < 7\ \text{Å}^{-1}\) is too limited for extracting any reliable structural information. This situation will change in the future, with the availability of hard X-ray free electron lasers (FELs) [220–229], where the number of photons per electron pulse will reach values as high as \(10^{12}\), compared with \(10^{6}\) for third-generation synchrotron radiation sources.

(e) Photo-induced pyridine substitution in \(\text{cis-}[\text{Ru(bpy)}_2(\text{py})_2]^ {2+}\)

The majority of systems investigated using TR-XSS was selected for their relevant photophysical/photochemical properties, but also for their high scattering power. A challenge for the TR-XSS technique is to extend its use to detect photoprocesses involving the release of multi-atomic fragments formed by low-Z atoms such as, for example, C, N and O. For these reasons and for our interest in the photochemistry of Ru–diimine complexes [86,230–233], we investigated, by TR-XSS, the ligand photodissociation reaction of the model compound \(\text{cis-}[\text{Ru(bpy)}_2(\text{py})_2]\text{Cl}_2\) in aqueous solution (20 mm solution, \(\xi = 1.1 \times 10^{-4}\)) [54]. This Ru–polypiridil derivative efficiently releases one pyridine ligand upon excitation of the metal-to-ligand charge-transfer (MLCT) band and subsequently coordinates a solvent molecule.

In our experiment, high-statistics data were collected using an aqueous solution of \(\text{cis-}[\text{Ru(bpy)}_2(\text{py})_2]\text{Cl}_2\) with time delays in the 800 ns to 5.5 μs range and exciting the MLCT band with an 800 ns long pulse of 532 nm light. The experimental conditions therefore can be considered quasi-static and provide a snapshot of the final stage of the ruthenium complex photodissociation.

Three TR-XSS simulated curves were calculated using a simplified scattering model and DFT-optimized structures for all the species involved in the photoprocess. In the first case, the \([\text{Ru(bpy)}_2(\text{py})_2]^ {2+} + \text{py}\) and \([\text{Ru(bpy)}_2(\text{py})_2]^ {2+}\) structures (M1) were used to model the transient and the unperturbed complex, while in the second case, the structures of the photocproducts \([\text{Ru(bpy)}_2(\text{py})(\text{H}_2\text{O})]^ {2+} + \text{py}\) and the unperturbed system \([\text{Ru(bpy)}_2(\text{py})_2]^ {2+} + \text{H}_2\text{O}\) (M2)
were employed, respectively (see figure 8). Finally, a small water cage was added to the photoproduct structure (M3), to roughly simulate the rearrangement in its solvation shell. Comparison between the three simulated curves, M1–M3, and the experimental curve (reported in the inset of figure 8) gives insights into the structural changes occurring to cis-[Ru(bpy)_2(py)_2]^2+ within the investigated photoreaction time range. Despite the limitations due to the simplified model employed in the description of the X-ray scattering signal and the intrinsic errors in the DFT bond distances, the agreement between M3 and the experimental curve indicates the dissociation of one py ligand and the coordination of a solvent molecule within 800 ns of excitation.

(f) Ultrafast X-ray absorption applications: a brief overview

Surprisingly, the first reported applications of TR-XAS concerned the solution photochemistry of bio-chemical macromolecules, which generally constitute an advanced and challenging research topic due to their high structural complexity. In a pioneering experiment, Mills and co-workers probed the reversible photodissociation of a CO group from carboxymioglobin via TR-XANES at the Fe K-edge [140,234–236]. Similar studies on related systems were reported by Clozza et al. [237] and by Chance and co-workers [141,238–240]. In addition, Chen et al. investigated the light-driven redox processes in an Fe–Zn diporphyrin integrated in a modified haem protein [241]. Employing an energy-dispersive set-up that allowed resolution in the ms domain, they succeeded in monitoring the Fe(III) → Fe(II) reduction process occurring upon photo-induced electron transfer from the Zn to the Fe centre, observing the time-dependent changes in the XANES features. Importantly, in all these cases, only continuous light sources were employed to pump the system in the ES, and the synchrotron X-rays were consequently used in a quasi-continuous fashion. This limited the best achievable time resolution to the µs time domain [28].

Significant advances in the techniques have been achieved over the past decade, taking advantage of new-generation synchrotrons and their unique properties (tunable emission, high brilliance, intrinsic time structure). The sub-ns time scale is nowadays routinely explored using third-generation synchrotron facilities. Strikingly, specially designed experimental arrangements...
(e.g. bunch slicing schemes) are able to lower the time resolution to a few hundreds of fs [160].

Of much interest to the scope of the present work, recent applications of ultrafast XAS spectroscopy mainly focused on compounds containing transition metal atoms, often studied in the solution phase. TR-XAS has been developed and implemented as a reliable tool to investigate the electronic and molecular structure changes of light-induced short-lived intermediates in solution with special attention addressed to reactions involving transition metal complexes [25,142,242–244]. Indeed, the rich transition metal photochemistry involving rearrangements of d-electrons and related structural modifications perfectly matches the combined electronic–nuclear information provided by TR-XAS at the ultrafast time scale [25,28,157,243–245].

For instance, the MLCT state structure of [Cu(dmp)]2+ in acetonitrile [149,246,247] and the structural changes resulting from an intramolecular electron-transfer process in [Ru(bpy)3]2+ [148,162] were elucidated. Furthermore, TR-XAS spectroscopy has been employed to study the structural distortions in the triplet ESs of two binuclear Pt-complexes, i.e. the Pt-POP system (see also §4d) [159] and the [Pt(ppy)(μ−tBu2pz)]2 (ppy = 2-phenylpyridine; tBu2pz = 3,5-di-tert-butylpyrazolate) complex [248]. Several studies concerned the structural dynamics of photodissociated intermediates in the solution phase as in the case of NiTPP-L2 and NiTMP (where TPP = nickel tetraphenylporphyrin, L = piperidine and TMP = tetramesitylporphyrin) [249,250]. Furthermore, TR-XAS was employed to monitor ultrafast spin crossover in iron complexes, unveiling also the structures of elusive high-spin states [160,251–253], as well as to clarify the mechanism of solvent-shell rearrangements around atomic ionic solutes [254].

Selected key TR-XAS studies that tackle different aspects of the solution-phase photochemistry of transition metal complexes will be hereinafter described in greater detail.

(g) Structural dynamics of photodissociated intermediates in the solution phase: the case of Ni-porphyrins

Metalloporphyrins have been widely studied, both experimentally [255–260] and theoretically [261–263], due to their application as versatile substrates in various technologically relevant light-driven processes, e.g. in the fields of light harvesting and photocatalysis [264–267]. Photoactivity in these compounds is generally triggered by light-induced rearrangements in the electronic structure, which promote ligation/de-ligation of a substrate via an electron-transfer mechanism [266]. Chen and co-workers studied the photodissociation of NiTPP-L2 (where NiTPP = nickel tetraphenylporphyrin and L = piperidine) by TR-XAS with ns time resolution [142,242]. This experiment, dating back to 2001, first demonstrated the potential of synchrotron-based laser pump X-ray probe TR-XAS measurements in unveiling transient molecular structure in disordered media.

The pathway for the reversible NiTPP-L2 photodissociation reaction is shown in figure 9a. The octahedral GS T0 is promoted to the upper triplet state T* and then rapidly passes to an excited singlet state S* via intersystem crossing. The S* state ejects two ligands giving the NiTPP intermediate and relaxing to a lower state with square-planar geometry, namely S0. When the reaction occurs in not-coordinating or weakly coordinating solvents, the photocycle is completed. However, in the case of coordinating solvents, the S0 state is stabilized by coordinating two solvent molecules and restoring the octahedral coordination to give the NiTPP-L2 T0 GS structure. Before this groundbreaking experiment by Chen and co-workers, no information was available on the S0 → T0 recombination mechanism and possible transient species involved. Several possibilities were proposed, e.g. a concerted axial chelation with two piperidine solvent molecules or a penta-coordinate NiTPP-L intermediate with square-pyramid geometry. Chen and co-workers addressed such issues acquiring XAS data on laser-pumped NiTPP-L2 in piperidine after 14 ns from optical laser excitation, and comparing the time-resolved spectrum with GS static XAS signals from NiTPP-L2 and a photostable form of NiTPP (see
Figure 9. (a) Reaction path for photodissociation of NiTPP-L$_2$. (b) Normalized static Ni K-edge XANES spectra for GS structure of NiTPP-L$_2$ and NiTPP (grey curves) and TR-XANES data for the laser-pumped sample after 14 ns from laser excitation (black curve). (c) EXAFS spectra obtained from Fourier transform of $k^2 \chi(k)$ curves for NiTPP-L$_2$ and NiTPP in their GS structure and laser-pumped NiTPP-L$_2$ sample: same curve codes as in (b). Reproduced with permission from [142]; copyright AAAS 2001. (Online version in colour.)

In particular, the shoulder found at ca 8340 eV in the XANES spectra reported in figure 9b, distinctly visible in the spectra of the laser-pumped and GS NiTPP, and not observed for the octahedral NiTPP-L$_2$, is assigned to the 1s$\rightarrow$4pz transition in square-planar geometry [268]. The XANES spectrum of the laser-pumped solution is well reproduced by a combination of GS NiTPP-L$_2$ and NiTPP-like spectra approximately in a 7:3 ratio, thus leading the authors to conclude that a transient square-planar NiTPP-like structure was being generated. The possibility of a penta-coordinate intermediate was further discarded by the absence of the pre-edge peak related to 1s$\rightarrow$3d transition in the laser-pumped spectrum, as expected in the case of square-pyramid NiTPP-L structure. Furthermore, analysis of EXAFS data reported in figure 9c showed that the average distance from the Ni centre to the nearest neighbour nitrogens falls between the values of ca 2.10 Å and 1.92 Å, found for GS structures of NiTPP-L$_2$ and Ni-TPP, respectively. The first-shell EXAFS signal can be best reproduced combining these two Ni–N distances with a relative ratio of 3:1, in good agreement with XANES data.

The same research group investigated the photocycle, the ES electronic/structural features and the ligation mechanism for another Ni-porphyrin, namely nickel-tetramesitylporphyrin (NiTMP). Combination of TR-XAS and optical transient absorption techniques allowed one to fully characterize the T$_1$ short-lived ES of NiTMP (200 ps lifetime), monitored in not-coordinating toluene to exclude the axial ligation process [249]. The ES electronic configuration was determined from analysis of the XANES features: singly occupied 3d$_{x^2−y^2}$ and 3d$_{z^2}$ molecular orbitals (MO)s separated by ca 2.2 eV in energy were identified, together with a 1.5 eV energy shift of 4pz orbitals with respect to the GS case. The molecular structure refined via EXAFS fitting is characterized by an expanded porphyrin ring with elongated Ni–N and Ni–C bonds, suggesting that a more planar conformation of the macro-cycle is adopted in the ES. These insights set the bases for a more comprehensive work where the photo-induced structural dynamics of the same NiTMP ES was monitored during the axial ligation process with pyridine ligands [250]. For the sake of comparison, the same process was investigated also in the case of the GS NiTMP, where ligation occurs from the S$_0$ state. Ni K-edge XANES spectra collected in the GS showed a pronounced broadening of the feature related to 1s$\rightarrow$3d$_{x^2−y^2}$ transition, evidencing a large range of 3d MO energies. The broad distribution of 3d energy levels is the key factor yielding ligation also from the S$_0$ state of the unexcited NiTMP; in a similar situation, transient degeneracy of the 3d$_{z^2}$ and 3d$_{x^2−y^2}$ MOs can easily occur, thus producing transitional vacancies in the first MO, which promote axial ligation in coordinating solvents. The effect of the photo-excitation is exactly the same, i.e. producing vacancies in the 3d$_{z^2}$ orbitals, resulting in a substantial increase of the axial-ligated photoproduct concentration.
Figure 10. (a) Investigation of MLCT ES for [Ru(bpy)_3]^{2+}. Left-hand panel: simplified energy-level scheme illustrating the photochemical cycle of [Ru(bpy)_3]^{2+}. Middle panel, from top to bottom: GS XAS spectrum of aqueous [Ru(bpy)_3]^{2+} in the Ru L_{2,3}-edges region (solid black line) together with the fit results for key XANES features (grey and green bands) and edge step (solid blue curve); experimental transient XAS spectrum collected at a 50 ps time delay (red points), and best-fit curve (blue solid line). Right panel: comparison of the transient spectra at 50 ps (red) and 70 ns (blue, scaled by a factor of 4.8) time delays; the inset shows a zoom of the EXAFS region. In addition, pseudo-radial distribution functions for the GS and ES complex (black line: experimental, red line: best fit) obtained from EXAFS analysis are reported at the bottom. (b) Investigation of MLCT ES for [Cu(dmp)_2]^{+}. Left-hand panel: reaction mechanism for photo-induced MLCT excitation of [Cu(dmp)_2]^{+} in solution elucidated using TR-XAS. Middle and right-hand panels: XANES and EXAFS spectra of [Cu(dmp)_2]^{+} in solution of toluene and acetonitrile, with (full circles) and without (black solid line) laser illumination. Parts of this figure are reproduced with permission from [162] (copyright ACS 2002), [246] (copyright ACS 2003) and [149] (copyright ACS 2010). (Online version in colour.)

(h) Ultrafast structural characterization of charge-transfer states in [Ru(bpy)_3]^{2+} and [Cu(dmp)_2]^{+} complexes

The triplet \(^3\)MLCT electronic and molecular structure of the prototypic complex [Ru(bpy)_3]^{2+} has been successfully probed by Chergui and co-workers [162] by TR-XAS at the L_{2,-} and L_{3,Ru}-edges. Excitation of the visible MLCT band of [Ru(bpy)_3]^{2+} leads, after efficient intersystem crossing, to the formation of the \(^3\)MLCT state, which then decays to the GS non-radiatively through several ESs (among which a metal-centred state) and radiatively with a luminescence lifetime of ca 600 ns, as shown in figure 10a, left-hand panel. Collecting XAS spectra at 50 ps and 70 ns, the authors observed significant changes in both the XANES and EXAFS regions (figure 10a, middle and right-hand panels, respectively). They found that in the ES, there is a contraction of ca 0.03 Å of the average Ru–N distance with respect to the GS structure. Since the D_3-symmetry was used to model the data, it is likely that the value found might reflect the average of non-equivalent bond contraction. Moreover, XANES line shape simulation and analysis pointed to a small increase (0.013 eV) in the D_3 field splitting in the \(^3\)MLCT state, consistently with the shortening of the metal–ligand bonds [269].
Chen et al. investigated the MLCT dynamics and solvation effects in a Cu(I) diimine complex by TR-XAS [25,149,246]. Franck–Condon light excitation of [CuI(dmp)2]2+ (where dmp is 2,9-dimethyl-1,10-phenanthroline) promotes charge separation to give a Cu(II)* centre and a reduced dmp ligand. The Cu(II)* ion with d⁹ electronic configuration is susceptible to Jahn–Teller distortion and forms an intermediated MLCT state with flattened geometry. A combination of optical spectroscopy, theoretical calculations and TR-XAS shows that such a state evolves in a penta-coordinated MLCT with electronic and structural features that depend on the solvent. In toluene, the MLCT state is luminescent at room temperature and has lifetimes ranging from several tens to over 100 ns. In contrast, the MLCT state is almost non-luminescent and has lifetimes as short as a few nanoseconds at room temperature in acetonitrile. Within 100 ps from laser excitation, the XAS signal in both solvents showed clear differences compared to the static XAS. In the XANES region (see figure 10b, middle panel), the intensity of the pre-edge peak is drastically reduced as a result of the conversion [CuI(dmp)2]2+ → [CuII(dmp)2]2+ and loss of the contribution from the 1s → 4pz transition. This feature evidences the transformation from coordination four to coordination five or six where the 4p⁰ orbital is delocalized and gives a less pronounced band. EXAFS analysis of the ES structures in acetonitrile and toluene (see figure 10b, right panel) highlights that in both cases, there is an increase in the coordination number. Moreover, it is observed that the Cu–N distances are contracted (0.04 Å) in acetonitrile, while being elongated (0.07 Å) in toluene in comparison to the GS. Strikingly, TR-XAS evidenced that changes in the coordination number occurred also in toluene, which is thought to be a non-coordinative solvent. The Cu(II)* in the MLCT is formally a 17-electron system prone to addition of a fifth ligand. The formation of an MLCT-solvent adduct stabilizes the ES, increasing the efficiency of non-radiative decays. Such a result is in good agreement with the weaker luminescence in acetonitrile, since in this solvent, the interaction of the Cu centre with the solvent molecule is stronger. In the case of toluene, the MLCT-solvent adduct is not able to lower the ES energy enough to significantly quench its fluorescence.

(i) Structure of quintet high-spin state and spin-crossover dynamics in [Fe(bpy)₃]²⁺

A large class of widely studied Fe(II) and Fe(III) inorganic compounds undergoes interconversion between a low-spin (LS) and a high-spin (HS) configuration under the effect of an appropriate external perturbation [270]. For this reason, they are generally referred to as ‘spin-crossover complexes’ [271]. In particular, the spin flip process can be promoted by light excitation, via the light-induced excited spin-state trapping effect [272] with implications in a wide range of intriguing technological applications for these systems, e.g. in the magneto-optics field [273,274]. The complex interplay between nuclear, magnetic and electronic features induced in these molecular systems can be uniquely followed by the TR-XAS technique.

Typically, Fe polypyridil complexes exhibit pronounced elongation of the Fe–N (ligand) bond in the HS state upon population of eg orbitals with anti-bonding character. After excitation to ¹MLCT or ligand-field states, these Fe complexes convert to a long-lived quintet spin state ⁵T₂ with ca 100% efficiency [271]. Theoretical models developed for this class of compounds, however, do not indicate any direct relation between the ⁵T₂ state lifetime and lengthening of the Fe–N (ligand) bond [275]. The [Fe(bpy)₃]²⁺ complex with the shortest-living ⁵T₂ state (650 ps at room temperature) represented an ideal candidate to test structural analogies between short-lived ⁵T₂ states and longer-lived analogues previously investigated via ultrafast XRD and quasi-steady-state XAS [276–278].

Gawelda et al. succeeded in capturing the [Fe(bpy)₃]²⁺ ⁵T₂ ES geometry in aqueous solution, probing the photoprocess with 70 ps hard X-ray pulses [251]. Fe K-edge TR-XAS spectra with ps resolution were collected to follow the structural relaxation from the HS to the LS state over the entire lifetime of the ES. A ⁵T₂ structure with an Fe–N bond distance 0.2 Å longer than the GS was obtained in this way. Interestingly, a 0.2 Å elongation is fully comparable with values found for other Fe(II) spin-crossover compounds characterized by longer-lived quintet ESs, as suggested by theoretical studies.
Figure 11. (a) Relaxation cascade as determined by ultrafast laser spectroscopy upon excitation of aqueous $[\text{Fe}^{II}(\text{bpy})_3]^2^+\text{ at 400 nm}$ [279]. (b) Top panel: Fe K-edge XANES spectrum of the LS state of aqueous $[\text{Fe}^{II}(\text{bpy})_3]^2^+$ (black trace) and of the HS quintet state (red dots). The latter is determined from the LS spectrum and the transient spectrum (see bottom panel) measured at a time delay of 50 ps after laser excitation at 400 nm. Bottom panel: transient XANES spectrum (obtained as the difference between the XAS signals of laser-excited and unexcited samples) recorded 50 ps after laser excitation at 400 nm (red dots) [251]. Note the increase in absorption at the pre-edge peak, labelled as 'B'. The blue stars represent the transient spectrum recorded at a time delay of 300 fs in the later work by Bressler et al. [160]. (c) The time scan of the signal (blue points) at the B feature, as a function of laser pump/X-ray probe time delay. Inset: long time scan up to a 10 ps time delay. The red trace is the simulated signal assuming a simple four-step kinetic model, $^1\text{A}_1 \rightarrow ^1\text{MLCT} \rightarrow ^3\text{MLCT} \rightarrow ^5\text{T}$, to describe the spin-conversion process.

Reproduced with permission from [160]; copyright AAAS, 2009. (Online version in colour.)

From the 50 ps transient data collected by Gawelda and co-workers, a significant decrease in intensity for the pre-edge peak of the transient XAS signal (labelled with 'B' in figure 11b) is evident. Such a feature is very sensitive to the Fe–N bond, as demonstrated by simulations performed within the multiple-scattering theory framework [280]. Bressler and co-workers employed a sophisticated bunch slicing scheme to obtain fs-hard X-ray pulses and monitor the time evolution of the pre-edge band in the earlier stages of the spin-conversion process [160]. Observing the signal stabilization in the time scan of the XAS intensity in this region, the authors found that population of the $^5\text{T}_2$ occurs within 150 fs from laser excitation. This evidence was further confirmed by collecting a complete transient XANES spectrum at a time delay of 300 ps, which matched well the 50 ps data from the earlier study by Gawelda et al.

These results are unprecedented in terms of time resolution and brilliantly solved the long-standing controversy on the quintet HS state mechanism of formation in Fe(II) complexes [271,281,282]. A three-state relaxation cascade, $^1\text{A}_1 \rightarrow ^1\text{MLCT} \rightarrow ^3\text{MLCT} \rightarrow ^5\text{T}$, was identified where the $^3\text{MLCT} \rightarrow ^5\text{T}$ transition occurs in a time scale corresponding to the period of the Fe–N stretch vibration [276].

5. Conclusions

TR-XSS and TR-XAS, now available with third-generation synchrotron radiation sources, are extremely powerful techniques for the characterization of ES transient structures. They have been successfully applied to a variety of chemical and biological systems revealing unique structural information on their photoprocesses, e.g. bond breaking, and ternary and quaternary rearrangements in macromolecules.

In the case of metal complexes, TR-XSS and TR-XAS have been able to capture rearrangements in the metal coordination sphere occurring within ps–µs from light excitation. This has allowed one to spot key intermediates and to disclose the ES dynamics governing the photochemistry of metal complexes. Furthermore, TR-XSS and TR-XAS data can be strategic to validate ES structures predicted by computations (e.g. DFT), providing control on the performance of theoretical approaches. Although still rare, such work can significantly advance the use of calculations in the study of photochemical reaction mechanisms. Moreover, accurate prediction of metal complex
photochemical behaviour can be employed to effectively guide the synthesis of photoactive
derivatives with technological and medicinal applications.

The availability in the near future of hard X-ray FEL facilities [220–229] will represent
an impressive improvement in the potentials of both TR-XSS and TR-XAS techniques,
both in terms of photon flux (moving from $10^6$ to $10^{12}$ photons per electron bunch) and
ultimate time resolution (the typical bunch width moving from $10^{-10}$ down to $10^{-14}$ s). The
development of adequate measurement techniques and data-acquisition schemes for measuring
X-ray scattering/absorption data at FELs will be essential to derive full benefit from these
new-generation photon sources.

In the time period between the acceptance of our manuscript and its publication, a few new
articles of high relevance to the topic discussed here have been published. A brief note is therefore
needed.

We determined the $^3\text{MLCT}$ ES structure of cis-[Ru(bpy)$_2$(py)$_2$]$^2^+$ and complemented our
previous TR-XSS characterization with a 100 ps resolution TR-EXAFS experiment performed at
the 11-ID-D beamline of the APS (see §4d) [283].

The results on the spin-crossover dynamics in [Fe(bpy)$_3$]$^2^+$ reviewed in §4i have been
confirmed and extended, exploiting the unique capabilities allowed by XFELs sources. The
experiment demonstrated the feasibility of ultrafast XAS at X-FELs with sub-100 fs time
resolution [284]. Finally, the same Fe-complex was selected to successfully test the feasibility
of hard X-ray emission spectroscopy, along with resonant inelastic X-ray scattering using the
pump-and-probe scheme [285].

L.S. gratefully acknowledges the MICINN of Spain for the Ramón y Cajal Fellowship RYC-2011-07787. E.B.
thanks INSTM for her PhD grant.

References

1. Harris AL, Brown JK, Harris CB. 1988 The nature of simple photodissociation reactions

2. Oregan B, Gratzel M. 1991 A low-cost, high-efficiency solar-cell based on dye-sensitized

3. Evans RC, Douglas P, Winscom CJ. 2006 Coordination complexes exhibiting room-
temperature phosphorescence: evaluation of their suitability as triplet emitters in organic


8. Erkkila KE, Odom DT, Barton JK. 1999 Recognition and reaction of metallointercalators with


10. Shank CV. 1986 Investigation of ultrafast phenomena in the femtosecond time domain.


38. Waller I. 1927 The transition from ordinary dispersion into Compton effect. Nature 120, 155–156. (doi:10.1038/120155a0)

39. James RW. 1948 The optical principles of the diffraction of X-rays. London, UK: G. Bell and Sons Ltd.


208. Stiegman AE, Rice SF, Gray HB, Miskowski VM. 1987 Electronic spectroscopy of d$_8$–d$_8$ diplatinum complexes - 1A$_2$($d\sigma^*\rightarrow p\sigma$), 3E$_u$($d_{xz},d_{yz}\rightarrow p\sigma$), and 3,1B$_2$u($d\sigma^*\rightarrow d_{x^2−y^2}$) excited-states of Pt$_2$(P$_2$O$_5$H$_2$)$_4$$^{-4}$. *Inorg. Chem.* **26**, 1112–1116. (doi:10.1021/ic00254a029)


