On the interplay between charge, spin and structural dynamics in transition metal complexes†

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This perspective presents some recent results concerning ultrafast intramolecular relaxation processes in metal-based molecular complexes. Ultrafast electronic/vibrational relaxation at sub-vibrational time scales, ultrafast intersystem crossing processes and ultrafast structure changes are discussed, stressing the questions that still need to be solved in order to arrive at a rationale that describes these processes. We will also discuss some new techniques, based on core-level spectroscopies that can provide new insights into the ultrafast intramolecular relaxation in these systems.

I Introduction

Over the past few years, metal based molecular complexes have attracted much interest due to their remarkable photophysical properties and the versatility with which these can be tuned by proper engineering of the ligands.1–3 The outcomes of the optical excitation are radiative decay and non-radiative intramolecular relaxation processes such as internal conversion (IC), intersystem crossings (ISC, i.e. a spin change) and intramolecular vibrational redistribution (IVR), which in most cases are accompanied by structural modifications. Some (often the fastest) of these non-radiative processes are mediated by conical intersections, which occur whenever two potential energy surfaces cross.4 Understanding the photo-induced dynamics of metal complexes is of great importance, not only for their fundamental aspects but also for the design and development of new molecular photonic materials or for their use in photochemical reactions.

Efficient electron transfer (ET) and charge separation in metal complexes are essential requirements for the optimal storage and conversion of energy by chemical means as well as for operation of nanoscale devices.5–8 The ET rates are as important for efficient and error-free operation of molecular devices, as they are, for example, in plant photosynthesis.9 Organic Light Emitting Devices (OLED) are another area where transition metal complexes play an important role, such as in the case of phosphorescent light emitting diodes (PHOLEDs).10 Their emission energy can be finely tuned by properly engineering the ligands bound to the metal atom,11–14 while the excited state radiative rate is altered by a proper mixing of the metal-to-ligand-charge-transfer (MLCT) excited states with low-lying triplet ligand-centred (LC) excited states. Evolution from the initially accessed singlet 1MLCT state to the spin-mixed 3MLCT state occurs by ISC, and efficient design of new OLEDs requires a detailed understanding of these spin dynamics.

All the processes discussed above (IC, ISC, IVR and structural changes) occur on ultrashort time scales, often in a competing fashion. In addition, for a large class of metal complexes, the initial trigger is a charge transfer process. Although there has been an increase in experimental15–32 and theoretical33–40 studies aimed at describing the interplay between the charge, spin and structural dynamics, many aspects are still unclear to this day. Furthermore, the origin and the parameters that govern the spin dynamics in metal complexes represent a wholly unexplored field. The presence of the metal atom undoubtedly causes spin changes that are orders of magnitude faster than in organic molecules, but it is now clear that the large spin–orbit coupling (SOC) constant of the metal is not the only parameter that...
governs the ISC rate, as we will see below. The origin of this large diversity in spin dynamical behaviour has remained an enigma to this day. Structural parameters and the nature of the initially accessed excited state, MLCT, LC or metal-centred (MC) may also have an influence.

At this point, there is no clear rationale that explains these trends and it is difficult to disentangle the various competing processes that occur in metal complexes. In this article, after a brief introduction to ultrafast techniques used to probe the relaxation processes in metal complexes, we will present results that are mainly aimed at highlighting the pending open questions. In this sense, we do not aim at a detailed review of the literature since the advent of the ultrafast spectroscopic tools applied to the study of metal complexes. At the end of this Perspective, we will present some of the novel tools that could address these open questions.

II Experimental tools

Here we briefly present the two main tools that have so far been used to probe ultrafast electronic relaxation in metal complexes.

**Pump-probe transient absorption spectroscopy:** In transient absorption (TA) spectroscopy, a first femtosecond pulse (called “pump” pulse) excites the system at \( t = 0 \), which is then probed by a second pulse (called “probe” pulse) whose time delay with respect to the first is tuneable by means of optical delay lines.\(^{41,42}\) Ultrashort white light probe continua are generated by non-linear optical techniques, allowing a large spectral range to be probed\(^{20,42}\) and recently even at rather short probe wavelengths below 300 nm.\(^{23,43}\) In TA spectroscopy, the signal consists of different contributions: The ground state bleach (GSB, i.e. an increased transparency of the sample at the ground state absorption due to the depopulation of the ground state), a stimulated emission (SE) due to the fact that the probe pulse may dump the excited population to the ground state if its range covers that of the fluorescence, and excited state absorption (ESA) due to absorption of the probe light by excited states. In the latter case, the final state(s) is(are) not always known.

**Femtosecond resolved fluorescence:** This is a sampling technique that allows recording decays of the fluorescence with typically 100 femtosecond time resolution.\(^{44,45}\) Upon excitation of the fluorescence at \( t = 0 \) by the pump pulse, the fluorescence is collected by wide angle optics and focussed onto a non-linear crystal to be frequency mixed with the light from the so-called gate pulse whose time delay is tuneable with respect to the pump pulse. The evolution of the fluorescence decay can then be recorded by detecting the mixed frequency (up for sum frequency, down for difference frequency) as a function of pump-gate time delay. Most fluorescence up-conversion experiments are carried out with single wavelength detection, but recently new schemes have been implemented that allow the recording of entire fluorescence spectrum at each time step.\(^{46-48}\) The advantage of such a strategy is that it allows a better visualization of the complete relaxation cascade in the system. Fluorescence up-conversion is in principle simpler than TA, but it is limited mainly to bright states.

A point to note is that none of these techniques contains a signature of the structure, the spin or the charge transfer character of the excited state(s). These information are deduced from an \textit{a priori} knowledge of the excited states, which is derived from steady-state spectroscopy and/or from theory.

III Excited state dynamics

**III.1 Relaxation processes on sub-vibrational time scales**

There is a growing body of evidence, mainly gathered from ultrafast broadband fluorescence up-conversion studies, that the relaxation from the initially excited state to the emitting state can occur on extremely fast time scales.\(^{19,20,48,49}\) This is best seen in Fig. 1, which shows the fluorescence spectrum at zero time delay and the steady-state absorption spectrum of the \([\text{M(bpy)_3}]^{2+}\) (\(M = \text{Fe}, \text{Ru}\)) complexes (similar patterns were also obtained for asymmetric polypyridine metal-complexes\(^{49}\)). One can see that the time zero fluorescence occurs with a mirror-like image with respect to the absorption band, even though in both cases the excitation energy was at 400 nm. This means that the system becomes vibrationally cold on very short time scales. Indeed, as derived in ref. 49, based on the sub-30 fs lifetime of the fluorescence (due to ISC to the \(1\text{MLCT} \rightarrow 3\text{MLCT}\) state\(^{19,20}\), the relaxation from the initially excited vibronic state(s) to the emitting state was estimated to occur in \(<10\) fs. This however does not mean that the system becomes cold in such a short time. Indeed, although the fluorescence appears vibrationally relaxed, this is only so as far as the high frequency Franck–Condon modes (that account for the modulations in the absorption band of Fig. 1\(^{49}\)) are concerned. The excess energy must be stored in lower frequency (and optically silent) modes. Thus the sub-10 fs relaxation time accounts for non-radiative relaxation processes such as IC and IVR, but the former may well be mediated by several conical intersections\(^{3}\) in the manifold of singlet MLCT states. Considering that the highest frequency mode of these systems (1607 cm\(^{-1}\)) corresponds to a period of \(\sim 18\) fs, this implies that the dumping of their energy (of several quanta for a 400 nm

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**Fig. 1** Steady-state absorption spectra (dashed traces) showing the \(1\text{MLCT} \rightarrow 3\text{MLCT}\) absorption band (dashed traces) and time-zero fluorescence spectrum (solid traces) of [Fe(bpy)_3]^{2+} and [Ru(bpy)_3]^{2+} in water, excited at 25 000 cm\(^{-1}\) (black arrow). The horizontal arrows indicate the respective absorption–emission Stokes shift (from ref. 19 and 20).
excitation) into the bath of internal modes of the molecule, must take place is less than half an oscillation!

Further evidence for these ultrafast intramolecular relaxation processes came from our study of the low spin (LS, $S = 0$) to high spin (HS, $S = 2$) transition in $[\text{Fe}(\text{bpy})_3]^{2+}$ upon excitation of the $1\text{MLCT}$ state absorption band (Fig. 1). Fig. 2 shows the calculated potential curves of the system along the Fe–N coordinate of the spin change. The spin transition occurs from the photoexcited $1\text{MLCT}$ state to the $5\text{T}_2$ excited quintet (HS) state, which lies $\sim 0.8$ eV above the ground state and an equilibrium distance that is 0.2 Å larger than that of the ground state.33,36,51 By a combination of ultrafast optical and X-ray absorption spectroscopy techniques we showed that the $5\text{T}_2$ state is populated in $<150$ fs, via a $1\text{MLCT} \rightarrow 3\text{MLCT} \rightarrow 5\text{T}$ cascade.27 By probing the arrival of the population into the quintet state using its absorption in the UV near 310 nm, we found that a vibrational wave packet with a period of 255 fs (Fig. 3) was generated in the HS state.23 Because the system undergoes the above IC/IVR processes within the $1\text{MLCT}$ manifold followed by ISC to the $3\text{MLCT}$ states, the wave packet is not created by the laser pulses, but by the impulsive Fe–N bond elongation upon $3\text{MLCT} \rightarrow 5\text{T}$ ultrafast ISC. It is quite remarkable that the wave packet appears in a state that lies $\sim 1.5$ eV lower than the excitation energy. We repeated the experiment by exciting at 400 nm (2.3 eV above the minimum of the quintet state) where the absorption is due to an LC state, and still observed the same wave packet in the quintet state.49 More recently,52 we also pumped at 280 nm (3.6 eV above the minimum of the quintet state), where the absorption is due to an LC state, and still observed the same wave packet in the quintet state! Considering that a minimum of two vibrational modes need to be coherently excited in the quintet state in order to form a wave packet with a period of 255 fs, this implies that the non-radiative relaxation must occur and reach the quintet state in $<125$ fs. Putting together these results with those of ref. 49 indicates that intramolecular energy relaxation proceeds at extremely high rates in these metal complexes, and this may also be the case with organic molecules.46–48,53,54 Remarkably, the relaxation in metal complexes is ultrafast, regardless of the nature of the initially accessed states (MLCT, MC or LC). This obviously has a number of consequences on the spin and structural dynamics.
III.2 Disentangling singlet and triplet states

From the integrated cross-section of the $^1\text{MLCT}$ absorption band of $[\text{M(bpy)}_3]^{2+}$ ($\text{M} = \text{Fe}, \text{Ru})$ complexes (Fig. 1), we estimate a pure radiative lifetime of $\sim 10$ ns for the $^1\text{MLCT}$ state in both cases. On the other hand, low temperature studies yielded lifetimes of the lowest two emitting $^3\text{MLCT}$ states of 10 $\mu$s and 230 $\mu$s for $[\text{Ru(bpy)}_3]^{2+}$. Thus, the singlet and triplet nature of these respective states is clear, but the $\sim 10$ ns lifetime of the $^1\text{MLCT}$ state may suggest a slight lengthening compared to a fully allowed electric dipole transition (1–2 ns). This is likely the result of mixing with near-lying longer lived $^3\text{MLCT}$ states. That such a mixing occurs is supported by the appearance of a weak triplet absorption as a red shoulder to the $^1\text{MLCT}$ absorption band (Fig. 1), while Yersin et al.\textsuperscript{50} identified the vibrational structure of the triplet absorption in the low temperature absorption spectrum of $[\text{Ru(bpy)}_3]^{2+}$. The time-wavelength plot of the emission of the latter is presented in Fig. 4. It exhibits a short-lived (<30 fs) fluorescence centred at 565 nm, while the long lived triplet phosphorescence appears at 620 nm (just as the steady state phosphorescence band). Fig. 4 unambiguously distinguishes the $^1\text{MLCT}$ and the $^3\text{MLCT}$ emissions both in time and in energy. The remarkable point in this plot is that despite the strong singlet–triplet mixing in the region of the $^1\text{MLCT}$ manifold, the fluorescence is clearly separable from the phosphorescence.

III.3 Ultrafast intersystem crossings

Table 1 lists the time scales for ISC of various complexes ranging from first row to third row transition metal complexes. While most deal with systems having a single metal atom, we also give a few examples of bimetallic complexes. The striking feature of this table is the erratic trend in ISC times, which do not follow the trends expected on the basis of the SOC constants as complexes containing light atoms (e.g. Fe) exhibit much shorter ISC times than those with one or two heavier (e.g. Pt) atoms.

In the case of $[\text{Ru(bpy)}_3]^{2+}$, Tavernelli et al.\textsuperscript{56} used non-adiabatic linear response quantum mechanics/molecular mechanics (QM/MM) molecular dynamics simulations to calculate the evolution of the $^1\text{MLCT}$ states using a qualitative estimation of the SOC constants based on orbital symmetries. They found that ISC events can already take place within the first 40–50 fs of dynamics in good agreement with the experimental results. Although their calculation did not consider IVR/IC processes, the picture that emerges from these simulations is that these processes occur prior to ISC, as actually is explicit from the experimental results.

In the case of the diplatinum complex $[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]^{4+}$ (PtPOP), the ISC time scales are three orders of magnitude larger than for metal–polypyridine complexes, even though the molecule contains two metal atoms, whose SOC constant is more than one order of magnitude larger than that of Ru or Fe. The initially excited singlet state of PtPOP, $^1\text{A}_{2u}$ (Fig. 5), has a molar extinction coefficient of 33 500 M$^{-1}$ cm$^{-1}$,\textsuperscript{57} which is one order of magnitude smaller than those of dyes with fully allowed dipole transitions. One of the reason for this lower singlet absorption coefficient lies in the spin–orbit mixing of singlet and triplet states, which actually induces a weak absorption of the latter.\textsuperscript{57} This situation is to some extent similar to the case of the Fe– and Ru–polypyridine complexes, whose ISC times are however three orders of magnitude faster.

In the case of PtPOP (Fig. 5), the metal–metal interaction largely stabilizes the lowest-lying singlet and triplet $^1\text{A}_{2u}$ (dσ* → pσ) states compared to the corresponding d$_1$ → p$_2$ states in monomeric complexes. Furthermore, there is a large energy gap between the $^1\text{A}_{2u}$ states and higher-lying singlet and triplet states. This energetic isolation of the $^1\text{A}_{2u}$ states makes them electronically (except for the spin flip) and geometrically almost identical, which is corroborated by the similar shapes of their steady-state absorption and emission spectra at low temperature\textsuperscript{58} and, as shown in ref. 59, their very similar excited state absorption spectra. The Franck–Condon (FC) factors between the singlet- and triplet-state potential curves are therefore very small,
and a direct spin–orbit interaction between $^1A_{2u}$ and $^3A_{2u}$ is symmetry forbidden. Last, they are separated by a large energy gap. This is different from other metal complexes with ultrafast ISC rates, which often exhibit close-lying singlet and triplet states. In addition to this, the ISC rates of PtPOP are solvent dependent, and vary by a factor of three in the sequence dimethylformamide–water–ethanol–ethylene glycol. In ref. 59, we suggested that the ISC is induced by spin–vibrionic coupling with a higher-lying triplet state and/or (transient) symmetry breaking in the $^1A_{2u}$ excited state. The particular structure, energetics, and symmetry of the molecule play a decisive role in determining the relatively slow rate of ISC, despite the large Pt SOC constant.

Table 1 Intersystem crossing times of metal complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>ISC transition</th>
<th>Time</th>
<th>Spin–Orbit constant (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(acac)$_3$</td>
<td>$^4T_2$–$^2E$</td>
<td>&lt;100 fs</td>
<td>0.027</td>
<td>18, 62</td>
</tr>
<tr>
<td>[Fe(bpy)$_3$]Cl$^{2+}$</td>
<td>$^1$MLCT–$^3$MLCT</td>
<td>≤30 fs</td>
<td>0.050</td>
<td>20</td>
</tr>
<tr>
<td>[Fe(bpy)$_3$]Br$^{2+}$</td>
<td>$^2$MLCT–$^2$T</td>
<td>~130 fs</td>
<td>23, 25</td>
<td></td>
</tr>
<tr>
<td>[Fe(bpy)$_3$]I$^{2+}$</td>
<td>$^2$MLCT–$^2$T</td>
<td>~190 fs</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>[Pt(acac)$_2$]Cl</td>
<td>$^1$MLCT–$^3$MLCT</td>
<td>~220 fs</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>ZnTPP</td>
<td>$^1$MLCT–$^3$MLCT</td>
<td>≤30 fs</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td>RuN719</td>
<td>$^1$MLCT–$^3$MLCT</td>
<td>~150 fs</td>
<td>130 fs</td>
<td></td>
</tr>
<tr>
<td>RuN3</td>
<td>$^1$MLCT–$^3$MLCT</td>
<td>≤30 fs</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>Pt(thpy)$_2$</td>
<td>$^1$MLCT–$^3$MLCT</td>
<td>≤45 fs</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td>[ReX(CO)$_3$(bpy)]$^+$</td>
<td>Ligated to unligated myoglobin</td>
<td>~800 ps</td>
<td>91</td>
<td></td>
</tr>
<tr>
<td>(x = Cl)</td>
<td>$^1$MLCT–$^3$MLCT</td>
<td>7.4 ps</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>(x = Br)</td>
<td>$^1$MLCT–$^3$MLCT</td>
<td>4–160 ps</td>
<td>91</td>
<td></td>
</tr>
<tr>
<td>(x = I)</td>
<td>$^1$MLCT–$^3$MLCT</td>
<td>≤30 fs</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>(x = etpy)</td>
<td>$^1$MLCT–$^3$MLCT</td>
<td>≤45 fs</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>Pt acetylides complexes</td>
<td>$^1$A$<em>{2u}$–$^1A</em>{2u}$</td>
<td>50 to 2000 fs</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>Pt(thpy)$_2$</td>
<td>$^1$A$<em>{2u}$–$^1A</em>{2u}$</td>
<td>~50 fs</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>Pt(Br)$_2$</td>
<td>$^1$A$<em>{2u}$–$^1A</em>{2u}$</td>
<td>~150 fs</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>Pt$_2$POP</td>
<td>$^1$MLCT–$^3$MLCT</td>
<td>10–30 ps</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td>Mo$_2$(O$_2$C–9-anthracene)</td>
<td>$^1$MLCT–$^3$MLCT</td>
<td>~10 ps</td>
<td>96</td>
<td></td>
</tr>
</tbody>
</table>

Another interesting observation that goes counter to the expected trend is the case of halogenated Rhenium–carbonyl diimine complexes ([ReX(CO)$_3$(bpy)]$^+$, X = Cl, Br, I). In these systems, the HOMO and HOMO − 1 are Re-X π-antibonding in character. The dr(Re) contribution to these orbitals decreases from ~50% to ~30% on changing the chloride ligand for iodide. The pt(halide) contribution concomitantly increases from ~20% to ~56%. Excitation of the singlet charge transfer (CT) state leads to an ISC to the triplet CT state, but the transfer of charge occurs from the Re-X moiety to the bpy ligand, which is why these states have been termed Metal-ligand-to-ligand-charge-transfer (MLLCT) states. It was found that the ISC time slows down significantly from Cl to I (Table 1 and ref. 22), which goes counter to the expected trends based on the “heavy atom effect”. In ref. 22, we found that the ISC rates show a linear correlation with the Re-X vibration (Fig. 6). Such a correlation would suggest that some structural rearrangement is involved in the spin transition, which may have to do with the fact that the electron is withdrawn from the Re-X moiety and therefore the field of forces between the Re and the halogen is modified. The spin-orbit constant of the metal atom is also given. Basically, the system needs to explore its configuration space in order to find the right crossing between singlet and triplet states.

III.4 Charge and spin dynamics

The above discussion mainly concerned examples of ISC involving either two CT states, in the case of Ru-, Fe- and Re-complexes, or two MC (or d–d) states in the case of PtPOP which was found to undergo a relatively slow ISC. However, ultrafast ISC also occurs between MC states as was observed by McCusker et al. in the case of Chromium(III) complexes. They found that ISC from the $^4T_2$ to the $^2E$ state occurs in <100 fs, followed by vibrational cooling on a timescale of 1.1 ps. These studies also concluded that vibrational relaxation within the $^4T_2$ states is
slower than ISC to $^2E$. In a later study, following excitation into the $^3A_2$/ $^3T_2$ absorption, they observed vibrational coherences superimposed on the kinetics associated with excited-state evolution. They attributed the observed mode (at 164 cm$^{-1}$) to the reaction coordinate of the ultrafast intersystem crossing. This reaction coordinate is associated to C–O bond stretch vibrations that also involve large amplitude motions of the peripheral methyl groups of the ligand framework.

The largest spin changes ($\Delta S = 2$) have however exclusively been observed in Fe-complexes, and in these cases they involve an MLCT and an MC state. In the case of Fe–polypyridine complexes, the $^1$MLCT–$^3$MLCT–$^3T_2$ conversion occurs in $<150$ fs (Fig. 2). The steady-state studies, which were carried on low temperature crystals of Fe(ii) complexes, showed that upon excitation of either the $^1$MLCT or the $^1T_2$ states, the $^3T_2$ state was populated with a near-unity quantum efficiency. Of particular interest here is the fact that the spin transition from the initially excited $^1$MLCT state to the final MC $^5T$ state occurs in $<150$ fs, which is remarkably fast, and that it bypasses the intermediate $^1T$ MC states, contrary to previous predictions, despite the fact that they favourably cross the MLCT potential curves. It is not clear why the $^5T$ state is exclusively populated, especially considering that this implies a more dramatic spin transition. This issue has been much debated in the literature and different theoretical models have been proposed, but none really answers this question. The favourable crossing of the $^5T$ curve was proposed in ref. 36 but it is not satisfactory for the reasons mentioned above. The presence of a nearby $^3$MLCT state has also been proposed but it was disputed in more recent work. The picosecond Fe L-edge X-ray Absorption Spectra carried out by Huse et al. failed to establish whether the $^5T$ state has a more ionic character, which would explain it being preferred in the relaxation from the MLCT states.

Another category of complexes where similar large spin changes occur are porphyrins. In haemoglobin and myoglobin, the spin state changes from low spin ($S = 0$ or $1/2$) to high spin ($S = 2$) upon detachment of the diatomic ligand (O$_2$, CO, NO, etc.) that is bound to the Fe atom in the porphyrin, on a similar time scale as Fe(n–)–polypyridine complexes: $\sim150$ fs$^{13,65}$ It has been proposed that the ligand detachment results from an electron transfer from the porphyrin to the Fe atom, followed by a back electron transfer to the porphyrin. If this is the case, then we have a somewhat similar situation to the Fe–polypyridine complexes, except that the direction of the electron transfers is reversed.

However, as already mentioned above, steady-state studies upon direct excitation of the $^1T_1$MC state of Fe(n) complexes demonstrated a quantum yield of 100% for the population of the quintet state, even though these states have favourable curve crossings with the ground state, and in the case of the singlet states, the same spin. This remarkable directionality may also point to an ultrafast ISC to the quintet state, but in the absence of ultrafast studies upon direct excitation of the MC states, it is difficult to draw conclusions as to a difference or a similarity with the MCLT excitation. The spin-orbit constant of the metal atom is also given. Basically, the system needs to explore its configuration space in order to find the right crossing between singlet and triplet states.

IV New strategies

The above pointed to some questions that are still pending regarding issues of ultrafast intramolecular relaxation, spin and structural dynamics. Addressing these issues requires new tools that: (a) allow a very high time resolution (down to a few fs); (b) are spin, charge and structure sensitive; (c) can visualize optically silent states. Obviously a single technique cannot easily meet all these requirements, but a combination of techniques can address the pending questions. Already in the past few years, the development of ultrafast hard X-ray absorption spectroscopy helped answer some questions concerning the structure changes upon $\Delta S = 2$ spin transitions in Fe-complexes. In these studies, it was a combination of ps and fs X-ray absorption spectroscopy at the K-edge of Iron with ultrafast optical transient absorption and fluorescence up-conversion that allowed us to fully nail down the photocycle of the Fe(n–)–polypyridine complexes undergoing an ultrafast $\Delta S = 2$ spin change. Later, Huse et al. implemented ps$^{64}$ and fs$^{70}$ soft X-ray absorption spectroscopy at the L-edges of Fe. These is an important development because the L$_{2,3}$ edges correspond to p–d transitions, which are dipole allowed, and therefore, they can deliver detailed information about the electronic structure of the excited state. In addition to these core-level spectroscopies, new ones are emerging that will bring another degree of insight into the interplay between the charge, spin and structural dynamics in molecular systems. These are ultrafast X-ray emission spectroscopy and ultrafast ultraviolet photoelectron spectroscopy.

When a material absorbs an X-ray photon a hole is created in the photo-induced SCO process, two electrons end up in the $e_g$ orbital, while the MLCT excitation has displaced only one electron from the $t_{2g}$ orbital. It seems that the shuffling of the electron from the metal to the ligand and back to the metal may be a crucial parameter that speeds up the process.
to determine from which electronic state the core hole has been filled. This technique is complementary to XAS, as the latter gives information about unoccupied electronic states above the Fermi energy or HOMO (highest occupied molecular orbitals) for molecules, while XES provides information on occupied electronic states below the Fermi energy. For example, when a hole is created in the 1s orbital, it can then be refilled by electrons from the 2p and 3p states, or even by valence electrons. Emission from the 2p and 3p states \( (K_a \text{ and } K_b \text{ emission lines}) \) contains information about the oxidation and spin state of the absorbing atom. This is due to the overlap between the 2p (3p) wave functions with the 3d states, resulting in remarkable sensitivity to the chemical environment. In metal complexes, the valence-to-core transitions originate from states that can be ligand-dominated, providing a detailed map of the valence orbital distribution, including covalency and ligand identity.\(^{71-73}\)

Recently a pump-probe scheme was implemented at the Swiss Light Source in which the changes of the XES spectrum of a metal complex were monitored tens of ps after laser excitation at 1 kHz.\(^{74}\) This first experiment represented a breakthrough because count rates are very low in XES. With the newly developed pump-probe scheme at MHz repetition rates,\(^{75}\) we can now increase the signal-to-noise ratio by more than an order of magnitude making ps XES experiments easier. The advent of X-ray Free electron lasers, which provide 6 orders of magnitude higher flux at sub-ps time resolution, will allow another significant increase in signal-to-noise ratio and time resolution for ultrafast XES experiments.

Photoelectron Spectroscopy (PS) is a powerful tool for the study of the physical and chemical properties of materials (mostly their surfaces). Core electrons are emitted by the sample due to the well-known photoelectric effect. The emitted electrons have a kinetic energy equal to the difference of the X-ray photon energy and the binding energy of the electron. Hence for a known photon energy the conversion from kinetic energies of the electrons to binding energies is straightforward, thus enabling element identification. The chemical environment of an atom affects the strength with which electrons bind to it. Atoms associated with different intra- and intermolecular chemical environments produce photoemission peaks appearing at slightly different binding energies which is referred to as the chemical shift.\(^{76}\) The latter is in fact correlated with electron densities in the molecules.\(^{76}\) Therefore, the technique can provide information about the chemical environment or oxidation state of an element. Due to technical problems with (volatile) liquids in vacuum, liquid phase PS was only recently developed, after Faubel \textit{et al.} introduced the in-vacuum liquid-microjet technique.\(^{77,78}\) Since then, the chemical shift in the static PS approach has also been a particularly powerful observable for probing electron densities and molecular orbital energies in different liquid environments.\(^{79}\)

In the case of ultrafast UPS, the initial and final states and all processes affecting them are time-dependent. The time-dependent chemical shifts are governed by the complicated interplay of all states and processes involved. The technique has recently been applied to liquid water microjets with <6 eV probe pulses,\(^{80-83}\) but these merely probe molecular valence orbitals which are delocalised over the entire molecule. Only the Abel group reported PS with deep-UV probe pulses from a high harmonic generation (HHG) source.\(^{84-87}\) With 40–70 eV pulses they could probe the core levels of aqueous iodide and of Fe in aqueous Fe(CN)\(_6\). Although PS of liquids with deep-UV pulses poses some technical challenges, such as the low photon penetration depth and small electron escape length, these are not a problem as the relaxation cascades we are interested in are mainly intramolecular in their nature. Ultrafast UPS will thus enable tracing the evolution of orbitals and their nature as a function of time in the course of the intramolecular dynamics. Of importance here is the detection of dark states, which are not amenable to observation by ultrafast optical techniques. Another advantage of UPS is that because the VUV radiation is produced by an HHG source, significantly shorter pulses can be generated (below 10 fs and even into the attosecond regime), which will allow very fast relaxation processes such as those described in Section III.1, to be probed in real-time.

In summary, recent years have witnessed a range of new experimental and theoretical tools that have generated a wealth of new information about the ultrafast photo-induced dynamics in metal complexes. At the same time, new questions have appeared which can be addressed by a variety of emerging ultrafast core-level spectroscopies.

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References
