Single-crystal X-ray diffraction studies of photo-induced molecular species

Jacqueline M. Cole*

*Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK
CB2 1EW. E-mail: jmc61@cam.ac.uk; Fax: +44 (0)1223 336362; Tel: +44 (0)1223 336300*

This *tutorial review* gathers together the recent developments in single-crystal X-ray diffraction that are starting to enable one to quantify directly the nature of light-induced electronic perturbations in chemical structures. Such structural information is key to understanding many photo-activated chemical processes and physical properties, and a description of the scientific impetus behind this incipient area of structural science, from academic and industrial perspectives, is given. Photoisomerism processes, solid-state photochemical reactions and spin-cross-over magnetic transitions, that have long-lived or irreversible light-induced states, are best understood by unravelling their three-dimensional structures measured *in situ* in their photo-converted state. A review of *steady-state* laser-induced single-crystal X-ray diffraction studies conducted, to date, and the experimental methodologies used in order to realise such structures, is presented. The structural characterisation of more transient photo-induced species (down to picosecond lifetimes) is paramount to a better understanding of the materials that undergo high-speed electronic switching, which make operative much of the electronics and optics industry, since there exists an inherent relationship between the excited-state structure and the physical properties exhibited. Prime examples include excited-state structures of molecular conductors and luminescent materials with potential applications as molecular wires, light-emitting diodes, non-linear optics, triboluminescence and electroluminescence. Previously, only indirect and qualitative interpretations of the nature of these excited-states could be formulated *via* spectroscopic techniques, but the developments in ms–ps *time-resolved* laser pump, X-ray probe single-crystal diffraction techniques, described herein, are overcoming this barrier, affording results that are entirely quantitative *via* a three-dimensional structural representation. In this regard, a review of structures of transient species studied to date is presented along with a discussion of the key experimental parameters that are required for a successful experiment, in terms of the X-ray, laser and sample characteristics. The importance of auxiliary spectroscopic work and complementary theoretical calculations is also briefly discussed. The paper concludes with a future outlook on new possible X-ray sources that will facilitate such work and extend it to structural studies on even more ephemeral species in the future.

1 Introduction

Photo-induced species occur in a myriad of compounds, ranging from those evident in nature, *e.g.* chlorophyll, through to technologically important materials such as photodarkening semiconductors and light-emitting-diodes. The photolysis process excites electrons into otherwise inaccessible states, thus inducing a redistribution of electrons within a molecule. In turn, this can lead to atomic displacement within the structure of the material or, more severely, isomerism or solid-state chemical reactions. A wide variety of photophysical properties unfold from these structural perturbations as these cause, for example, associated changes in dipole moments, luminescence or radical formation.

Jacqueline Cole graduated from the University of Durham with 1st class BSc honours in Chemistry in 1994. She subsequently undertook a PhD via a joint studentship between the University of Durham and the Institut Laue Langevin, Grenoble, France. Based in Durham for year 1, and France for years 2 and 3, her research focused on structure–property relationships in organic non-linear optics using single-crystal X-ray and neutron diffraction techniques. In 1997, she moved back to the UK to carry out two years of postdoctoral research in physics at the University of Kent at Canterbury, working on the microstructure of rare-earth phosphate glasses, materials that exhibit exotic optical and magnetic properties. In 1999, she moved to the University of Cambridge, having been awarded a Junior Research Fellowship at St. Catharine's College. Based in Chemistry, she conducted feasibility studies and test experiments on photo-induced species using time-resolved X-ray diffraction. During this period, she was awarded the first British Crystallographic Association Chemical Crystallography prize, in 2000, for her structural work on optical materials. In October, 2001, she took up her current post at Cambridge as a Royal Society University Research Fellow where she is primarily engaged in developing time-resolved single-crystal diffraction instrumentation and experimental methodologies for application to photonic materials. Away from the laboratory, she enjoys cycling, running, film, art, and doing a spot of recreational mathematics: in this capacity, she has just completed an Open University BSc (Hons) Mathematics degree.

Whilst photophysical properties can be fairly readily measured, their structural origins generally remain elusive since the photo-induced states are most typically very transient (µs or less). Recent developments in time-resolved experimentation have led to fairly routine methods for determining a certain level of indirect structural information, particularly from time-resolved optical and infra-red spectroscopy. However, more direct structural characterisation methods, such as EXAFS and diffraction techniques, have been hitherto confined to providing a time-averaged picture of molecules. Furthermore, the majority of the indirect structural information existing from time-resolved spectroscopy emanates from solution-based measurements, and yet, the physical property so often sought is aimed at solid-state devices. The resulting dearth of same phase comparisons between structure and property hamper implicitly their interpretation and use in understanding the role of structure in a given physical phenomenon.

Crystallography is the ultimate technique for determining the bond-geometry of a molecule with high accuracy and in a three-dimensional representation. Given that such structural characterisation is also undertaken using solid-state samples, crystallography would therefore seem to be the ideal technique with which to embrace the fourth dimension of time within its capabilities, such that one can understand photophysical processes. Indeed, many scientific processes in all disciplines evolve over time, and so a time-inclusive investigative power of crystallography is also attractive to many other areas of structural science. Consequently, the last few years have seen some pioneering time-resolved developments in all ranges of science. Time-resolved chemistry is evolving particularly rapidly, revealing results from a whole host of experiments of varying degrees of qualitative and quantitative nature and concerning processes with temporal variations spanning across a myriad of different time-domains.[1] Implicit within this evolution is the development of time-resolved crystallography.

The typically very transient nature of photo-induced processes makes this area of time-resolved crystallographic development particularly challenging, as do the many practical complications surrounding the optical excitation (see Section 4). Moreover, high atomic resolution is usually a prerequisite: in the majority of cases, the redistribution of electrons, caused by photo-induction, manifests itself in an associated change in the bond-distance between two or more atoms within a molecule. For example, a luminescent organometallic material will classically be photo-excited into a state which will affect metal–ligand charge transfer (MLCT). The primary structural perturbation in such a case will be a change in bond length between the metal and ligand(s) concerned. Similarly, an oxidation change may be brought about by photo-induction in a material and in such a case the coordination sphere about the metal ion will contract or expand according to the increase or decrease in oxidation number, respectively. Bond length changes of 0.1–0.2 Å would be typical, but this could be much smaller, particularly in organic compounds: C–C bond lengths are shorter than metal-containing bonds and so any changes are inherently harder to detect. Obtaining a sufficient level of atomic resolution to observe the structural perturbation sought thus presents a really major experimental challenge in this area. Ultimately, one would in fact wish to be able to collect data with high enough resolution to perform three-dimensional electron density distribution mapping *via* a full multipole charge-density refinement, although such studies are likely to remain beyond our capabilities for some time yet.

Several timely advances in synchrotron and crystallographic instrumentation have helped overcome some of these experimental challenges, and indeed, have made feasible the subject area of research. The advent of a new generation of synchrotrons across the world has brought with it much more enhanced

X-ray beam intensity, stability, reliability and efficiency, all so critical for this work. The commercialisation of charge-coupled device (CCD) area detector technology has revolutionised the whole of crystallography, not least time-resolved crystallography where the orders of magnitude decrease in data collection time has been critical for the developments described herein. Certain photo-induced processes occur or can be stabilised at very low temperatures. In these cases, the development of open-flow helium-based cryostreams has been instrumental in these developments. The recent revolution in laser technology has heavily facilitated the feasibility of this new area of structural science, with ns or ps-pulsed lasers now standard and all commercial lasers being designed for use as more modular bench-top 'turn-key operation' types of apparatus. The field of optical spectroscopy has also aided substantially the progress of this field since much of its highly advanced electronic timing technology is readily transferable to the subject area.

What follows is a review of the types of photo-induced processes in materials that are of interest, experimental methodologies presently being developed for photo-induced X-ray diffraction to study these processes, the results obtained so far from this work, experimental challenges and developments in this new area of research, and the future prospects of this technology. The review concentrates on the use of monochromatic oscillatory single-crystal diffraction methodology, necessarily restricting itself to chemical results although recognising, in places, important related Laue-based diffraction work from the biological sphere. It is also pertinent to add that important work, similarly aimed at affording direct and quantitative photo-induced structural information, is also being attempted using EXAFS spectroscopy, and one is referred to the reviews by Chen[2] and Saes *et al.*[3] and references therein for further details.

2 Types of photo-induced processes of interest in materials science

A deeper knowledge of the structure originating functionality of light-driven chemical processes is immensely important on account of the associated technological implication of such materials. Over the last few decades, the world has experienced an electro-optical revolution: digital light displays that light up car dashboards, mobile phones and stereo sound systems; fluorescent and phosphorescent screens, for example in portable computers; underwater lighting-equipment and night-working apparatus; optical switches and shock-wave triggers for use within electronic circuitry itself. The controlling light phenomena are all the result of electronic charge-transfer within a molecule or ionic displacement, and occur in various manifestations, be it light-induced fluorescence or phosphorescence, or electro-, tribol-, chemi- or sono-luminescence (the application of electric field, mechanical force, chemical reaction or sound waves, respectively, to produce light) which can produce either fluorescence or phosphorescence (*e.g.*, Fig. 1).

One of the implicit reasons why these phenomena can be used in electrical and electro-optical devices is the high-speed timescale on which these luminescent processes occur, since electronics require such fast reaction operating frequencies to ensure, for example, constant communication and screen updating. The majority of all fluorescent and phosphorescent processes occur, respectively, on the timescale of ns–ps or ms–µs.

There also exist many non-luminescent light-driven phenomena with very ephemeral photo-active states that are of high technological importance in the electrical or optics industry. In particular, conduction/insulator transitions in molecular species are of enormous interest in solid-state

Fig. 1 Application of electroluminescence in lighting up the display in this watch. An electric signal, caused by pressing the 'light' button on the watch, excites the molecules in the display medium that cause luminescence upon their relaxation.

physics. The phenomenon, which occurs typically on a time-scale of the order of fs–ns, is led inherently by structural change that results from perturbations in electronic charge-transfer of a molecule. Non-linear optical phenomena (*e.g.*, Fig. 2) occur
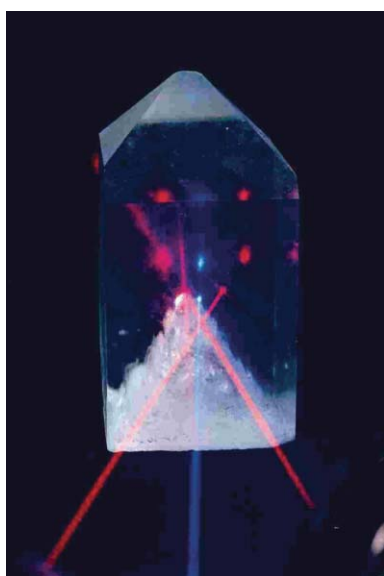

Fig. 2 A non-linear optical material, (ammonium dihydrogen phosphate), displaying second-harmonic generation, the frequency doubling of light (infra-red to blue). The origin of this physical phenomenon is entirely dependent on ionic displacement or molecular charge-transfer processes.

on similarly fast timescales and are governed by molecular charge-transfer processes and it is highly desirable to comprehend their *in situ* structural manifestations more fully.

Materials with much longer (ms–∞) light-driven lifetimes are generally non-luminescent but are also highly desirable industrially. Long-lived photodarkening properties have been long exploited in glasses. Indeed, it was this area of structural research that saw some of the first attempts at quantifying light-driven structural perturbations.[4] Better photodarkening materials are continually being sought for better device application, as are new long-lived photo-active compounds for possible use in new sunscreens (UV–vis protection), optical-storage and magnetic switches. Currently used photodarkening materials are typically inorganic and their application is usually based on exploiting the low energy band-gaps in these materials to absorb light.

Sunscreens exploit light in one of a variety of ways. Long-lived light-absorbant states are a key physical property in the application of one of these variants:[5] a suitable active material of a sunscreen would work by absorbing light into an upper layer of the skin, which undergoes a photochemical change, that in turn blocks UV-B penetrating to the more sensitive lower epidermis cells. The longevity of the light-absorbant state

ensures that this skin continues to remain protected for several hours or until the sunscreen is removed by washing or skin abrasion. Typically, the photochemical change involved is a photoisomerisation. Most other sunscreens work by absorbing light in the harmful UV–vis radiation band, and emitting it at a lower wavelength that is unharmful to the skin. In these cases, the light-driven lifetime is typically on the more ns–μs transient scale.

More generally, photoisomerisation occurs in many areas of organic and organometallic chemistry and can be reversible or irreversible. Despite its more applied nature, such as that described above, photoisomerisation processes can also be very important for the development of fundamental research. For example, they may comprise part of a new reaction mechanism in organic chemistry that is being developed for a given application, or maybe *hv* induction is being used to form a new chemical product. Photoisomerisation also occurs with great propensity in nature, for example, in signal transduction of photoreceptor proteins and photorepair processes and in photosystems 1 and 2 in plants. The structures of biological species are generally much harder to characterise than chemical materials, especially in their *in vitro* state, and the structural characterisation of their photoisomerised states and the associated photoisomerisation mechanisms are necessarily even more complex. This said, some pioneering work has been achieved in this direction; for example, see the work on photo-active yellow protein (PYP)[6] and a flavin-bound plant photoreceptor domain.[7] A better structural knowledge of all chemical photoisomerisation processes and their mechanisms will, however, undoubtedly provide a very useful insight to many of these biological processes. It is therefore a valuable goal to strive for the structural characterisation of all species undergoing light-induced isomerisation. Timescales of photo-isomerisation processes vary enormously, but many chemical photoisomerisation processes occur *via* metastable states (very stable under certain conditions such as reduced temperature) or irreversible transitions. In these cases, their crystal structure can be readily probed, pending the sample is not destroyed during the isomerism process.

The importance of good materials for optical storage cannot be understated given its importance in computing and memory hardware. In particular, there is presently an immense amount of commercial interest in developing holographic storage, hailed as the next generation of revolutionary storage media.[8] Holographic storage will allow three-fold data encryption onto a single point, thus exploiting the volume of a material rather than just its surface area, as used on a compact-disc (CD) or digital-versatile-disk (DVD) for example. Hologram memory can be created by focusing successive interference patterns of two light beams into a specific volume of a material. Each pattern relates to one page of data, coded as light and dark boxes on a screen, through which one of the incoming beams passes (the data carrying beam). The two beams have been split from a single laser source and so the second beam, which passes through no screen, acts as a reference signal (no data information) upon their coalescence. With the proposed ability to store over 100 times the data capacity of a DVD in a material the size of a sugar cube, the potential of this new medium is incredible (Fig. 3). However, developments are currently largely hampered by two factors. One problem lies in the stringent requirements of data retrieval: data are reconstructed by diffracting a further light beam, at *exactly* the same angle as the reference beam enters the material, onto a detector; an error of one millionth of a metre will render the data irrecoverable. The other problem is that there is a dearth of suitable materials for long-lived device application. Given the high speed of industrial drive in this area, it is critical that materials chemistry keep up with the technological developments and it will only do so

Fig. 3 A photo of 100 stacked DVDs and a sugar cube. If holographic storage lives up to its hype, one will be able to store a terabyte (1000 Gb) of data in a crystal the size of a sugar cube. Employing current commercial optical storage devices, a terabyte of data would fill more than 1000 compact disks, or over a 100 DVDs. The use of an actual sugar cube as a placebo here is a deliberate attempt to emphasise the fact that whilst the optical technology is developing rapidly, scientists are still struggling to find suitable materials for the application.

by understanding the structural manifestations of the light-processes ensuing the application. Inevitably, the optical etching created in the material needs to be as long-lived as possible, or else data will be lost irrecoverably over time. Therefore, photo-active materials with metastable lifetimes have enormous potential in this area.

Light-induced magnetic spin transitions have shown potential in electronic switching devices and magnetic data storage applications.[9] At a given temperature, the magnetic-spin active metal ion in the material (typically Fe) converts from the low to high-spin state upon the excitation of light of a certain wavelength. How sudden this phase transition is and how the hysteresis effect transpires dictates the level and usefulness of the 'bistability' of the material: a bistable material will exhibit a sudden phase transition and hysteresis that will allow the material to be able to exist in temperature phase space as either the high or low-spin magnetic spin-state, over a wide temperature range. The sudden phase-transition at a given temperature also renders these types of materials useful as a possible temperature sensor. The lifetime of the bistable state will correspond directly to the lifetime of any possible device in which it could be applied: any loss in definition of hysteresis for example could cause error in electronic switching or could corrupt data irrecoverably if such materials are ultimately used in magnetic storage media. It is therefore very important that materials with long-lived light-induced magnetic spin transitions are understood so that one can 'engineer' more suitable candidates, with more commercially viable operating temperatures (presently transitions are typically sub-50 K), and with greater longevity of bistability. Light-induced X-ray diffraction experiments would be very useful to achieve this goal since the crystal structure of a magnetic material in a given spin-state can be characterised by single-crystal X-ray diffraction.

There are undoubtedly many more photo-induced phenomena left undiscussed here but hopefully those described above give a fairly representative view of the wide scope of materials for which photo-induced single-crystal X-ray diffraction studies stands to provide key advances in these areas, thus underlying the importance of such crystallographic developments.

3 Four technological timescales of X-ray diffraction experiments

The lifetime of the photo-induced state in a given material dictates the type of instrumentation required for the determination of its structure. The shorter the lifetime of such a species, τ_o, the more challenging the experiment becomes. These instrumental challenges can be split into four categories: steady-state methods ($\tau_o >$ min), pseudo-steady-state methods (min $\geqslant \tau_o \geqslant$ ms), and stroboscopic methods using a pulsed X-ray source generated by means of either a mechanical chopper (ms $\geqslant \tau_o \geqslant$ μs) or accelerator physics (μs $\geqslant \tau_o \geqslant$ ps) methods.

3.1 Steady-state methods

For materials exhibiting very long-lived (hours) or irreversible photo-structural changes, *steady-state* methods are used whereby the photo-induced structure is obtained in three experimental steps: firstly, one determines the ground-state structure of the material using conventional small-molecule single-crystal X-ray diffraction methods; next, the crystal, still mounted on the X-ray diffractometer, is optically-pumped for several hours using a suitable light source, this typically being a flash-lamp (broad-band wavelength of light) or a laser (monochromatic source); the light-source is then removed and the resulting structure is determined, again using conventional X-ray diffraction methods, under the same experimental conditions as before. The resulting structure from this second data collection will comprise contributions from both the original ground-state and the light-induced structure. This is because the light-induced structure cannot be obtained experimentally in isolation since, in any photo-induction process, one will not generally achieve 100% photo-conversion in a single-crystal. In fact, one generally aims to obtain no more than 20–30% photo-conversion, since beyond this, the integrity of the crystal is endangered: if structural perturbations within a crystal lattice are too great or numerous, the crystal will fracture or explode. One can, however, effectively isolate the light-induced structure by analytical means. This is achieved by first importing the refined ground-state structural model, obtained using the data from the first experimental step, into the 'ground plus light-induced' refinement model as a fixed entity, except that all atomic coordinates are normalised to the unit cell parameters of the 'ground plus light-induced' state, to take into account their slight change that is expected on account of a small perturbation in the overall molecular environment by having two similar but not exact molecules now present rather than one type. A new scale factor is then refined against the 'ground plus light-induced' data and a 'photodifference' map thence obtained: this is essentially a Fourier difference map that reveals the photo-induced structure exclusively since the ground-state structure has already been accounted for by the normalised fixed coordinates (see for example, Fig. 4). The atomic positions of the photo-induced structure can therefore be located from this map using normal procedures for interpreting Fourier difference maps, and refined to produce the final combined 'ground plus photo-induced' model. The occupancy factor of all atoms in each component should be refined as a common factor with both factors summing to 100% (in exactly the same fashion as one would model molecular disorder) so that one can realise the percentage of photo-conversion achieved: the occupancy factor of the light-induced structure.

Since steady-state methods rely on the light-induced effect in a sample lasting for the duration of a single-crystal X-ray diffraction data collection that is complete enough to obtain a full structure determination, the intrinsic minimum sample light-induced lifetime that can be probed by steady-state
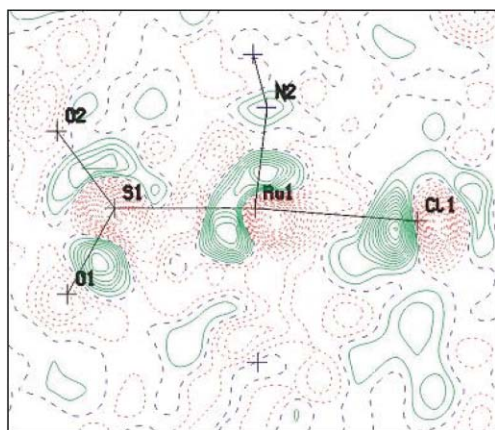
Fig. 4 A 'photodifference' map showing the ground-state (already modelled) depicted by the black lines together with the electron density associated with the light-induced [Ru(SO₂)(NH₂)₄Cl]Cl complex.[10,11] In this example, the SO₂ is the photo-active ligand, undergoing a η^1-SO₂ (end-on) to η^2-SO₂ (side-bound) photoisomerisation. The sulfur atom and one of the oxygens of the η^2-SO₂ bound ligand are evident in this Fourier difference map by the green peak and more diffuse green area, respectively, on the left of the figure (the other oxygen cannot be seen here as it lies out of the plane).

methods depends critically on the speed by which data collection can be undertaken. In turn, this is inherently dependent upon several factors: (i) the crystal symmetry of the sample. The higher the crystal symmetry, the more symmetry equivalent reflections that are afforded, and so smaller volumes of reciprocal space are needed to be covered in order to obtain a complete data set of unique (not symmetry-equivalent) reflections compared with a sample with lower crystal symmetry, *e.g.* a complete data set of unique reflections requires one quadrant of reciprocal space for an orthorhombic sample whereas a hemisphere is required for a monoclinic crystal. The smaller the area of reciprocal space that needs to be covered, the faster the data collection on account of the smaller the total number of frames of data that need to be collected, since there are less angular steps that the diffractometer needs to move through. (ii) Detector coverage, sensitivity and read-out time. It is generally agreed that without the recent advances in CCD area detector technology for X-ray diffractometers, this field of research would not be viable since the speed of data collection is so critical to these experiments. Developments in detector design are continuing at a revolutionary rate. Detectors with larger active areas are being developed which will afford greater coverage of reciprocal space per unit time. Strategies to increase detector response sensitivity are being investigated; achieving greater sensitivity will inevitably result in faster data collections and accessibility to many more data (previously too weak to observe above detector background). Detector read-out time is one of the major drawbacks of area detector technology as not only is it nearly always the time-limiting factor of the data collection speed, but it is so by a large margin. Substantial improvements in this area of detector development are required, without loss of detector sensitivity, before samples with much shorter intrinsic sample light-induced lifetimes than the present minimum can be studied using steady-state methods. (iii) X-ray diffraction intensity. The controlling factors here are the X-ray source and the crystal size of the sample. The brightest X-ray source will inevitably afford the most intense diffraction possible, and so one should consider carrying out the experiment at a synchrotron source if intensity is not sufficient using a laboratory source (either a sealed tube or, more intense, a rotating anode). Using a larger crystal will also yield more intense diffraction. However, one must ensure that the crystal is not so large that it will become impenetrable

to light. Given that the optical penetration depth in a sample can be very small (often of the order of μm) one often has to compromise heavily the crystal size, in terms of providing good intensity, to ensure successful photo-conversion, without which the experiment is rendered untenable. Indeed, those experiments where μm crystal-size restrictions are dictated optically are only viable at synchrotron sources. (iv) X-ray wavelength considerations. There are two competing factors here. On the one hand, a short wavelength is desirable since this improves the resolution of data collected to a given maximum scattering angle, 2θ. On the other hand, the shorter the X-ray wavelength, the greater the rate that the X-ray atomic form factor will fall off as a function of 2θ for any given element. Given the importance of resolution in these studies, owing to the subtle structural changes sought, one should aim for as short a wavelength as possible but without diminishing the X-ray form factor so much that the X-ray intensity falls beyond feasibility. These arguments assume a completely free choice of an X-ray wavelength band, but that is only available at a synchrotron source. In a laboratory, one is of course typically restricted to one or two wavelengths only, depending on the types of X-ray sealed-tube sources available, most commonly Mo ($\lambda = 0.71$Å) or Cu ($\lambda = 1.54$ Å).

In favourable cases (using a large strongly diffracting crystal of a sample with high optical penetration depth, high crystal symmetry, and collecting data at a synchrotron source using a moderately short wavelength) the present light-induced lifetime minimum limit for steady-state studies can be estimated to be about 20–30 min, based on the above considerations.

3.2 Pseudo-steady-state methods

Below this steady-state timescale limit, one can employ *pseudo-steady-state* methods, down to a sample light-induced lifetime of the order of ms. These methods allow a photo-induced state to be activated and maintained by continuously pumping the sample with an optical source that has a pulse frequency ('repetition rate') that repeats faster than the photo-induced lifetime. After an initial cycling period of optical-pumping, photo-saturation is achieved: the maximum possible percentage of photo-conversion within a sample, for the given optical pumping source (see Fig. 5). The sample remains in this
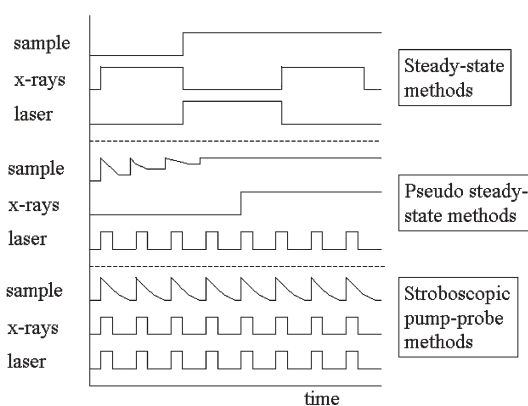

Fig. 5 A schematic diagram of the relative timing systems between laser, X-ray and sample photo-conversion lifetime. The nature of steady-state, pseudo-steady-state (in its simplest form) and stroboscopic pump–probe methods are illustrated. The absolute timing for each of these methods is on a different scale to each other: the whole experiment is shown for the steady-state methods; the pseudo-steady-state representation shows up to the beginnings of the first data-collection frame; the stroboscopic representation illustrates a regular pattern that occurs throughout the experiment. Stroboscopic pseudo-steady-state methods are not represented here, *per se*, but they essentially represent a combination of the basic pseudo-steady-state and stroboscopic methods shown here.

'pseudo-steady-state' throughout the experiment as long as the optical-source remains continuously pumping on the sample at its initial pulse rate. As with the steady-state methodology, there are several distinct steps to the experiment. In its simplest form, a conventional ground-state data collection can be first undertaken on the sample. Optical-pumping then commences and the same data collection routine is repeated once the sample has reached its pseudo-steady-state. Once the data have been collected, they can be analysed in a manner identical to that described above for steady-state methods.

For these types of experiments one must consider carefully the effects of laser heating on the sample during the data collection since the thermal effects may themselves affect a structural perturbation. Whilst such a change would generally be small, typically manifesting itself predominantly within the anisotropic displacement parameters of atoms in the structure, the light-induced effect sought may also be subtle. Therefore, if not accounted for, laser heating effects could readily disguise the light-induced effect sought, or worse, allow one to attribute erroneously a structural distortion to a photo-effect.

Heat capacity measurements on the sample could be used to calculate the expected temperature increase due to laser heating. One further data collection, post optical-pumping, could then be carried out at a sample temperature corresponding to the sum of the temperature of original data collection and the expected increase in temperature. Any structural differences due to laser heating could therefore be ascertained by comparing the structures relating to the original ground-state experiment and this final one and thence distinguished from any photo-effects. However, the accuracy of such temperature calculations may be compromised by the fact that the efficiency of the sample environment to dispel the laser heat away from the crystal is unknown since it will depend on a whole host of factors. For example, the temperature gradient between the laser and the sample environment, the level of thermal contact, flow, and heat capacity of the crystal cooling gas are important considerations. The associated changes in unit cell parameters can be accounted for by normalisation in a similar way to that described above for the steady-state methodology.

An alternative data collection methodology, that will circumvent some of the complications surrounding laser heating effects, involves collecting each frame of data from the ground and photo-induced states in an alternating fashion. Here, the usual data collection strategy is set-up for optimising angular coverage of reciprocal space, but at each angular setting, a data frame is collected twice, first without optical pumping, followed by a time-delay whilst the pseudo-steady-state is obtained by optical-pumping, and then again whilst the sample remains in its pseudo-steady-state. An electronic timing mechanism is set up between the laser shutter and the diffractometer control software such that this process can be repeated automatically. This procedure precludes the possibility of gradual build up of laser heating effects. Given the long detector read-out time of a data frame, there is negligible loss of experimental time by this methodology, if the time-delay for awaiting the pseudo-steady-state can be programmed to act in parallel operation to the detector read-out command process. Presently, however, such parallel operation is not standard in most diffractometer software although it is entirely possible.

Data interleaving strategies are also highly advantageous for minimising the danger of sample decay. In photo-induced crystallographic experiments, crystal fracture is a frequent occurrence during an experiment owing to the severe conditions to which the crystal samples are exposed: laser heating, sample cooling (often to helium-based temperatures), and intense X-ray sources (often synchrotron radiation). Moreover, if the optical penetration depth of the laser is such that the laser is not able to penetrate entirely through the crystal sample, local heating effects within the crystal will build up which cannot be dissipated by any route other than by crystal explosion. As mentioned earlier, if too much movement in the crystal lattice occurs as a result of the photo-conversion, this can also cause crystal fracture. If the crystal were to fracture half-way through an experiment where this alternating 'light-off/light-on' strategy was being used, at least half of a data collection could be analysed. However, there is little use in analysing a full ground-state data collection together with a ten-minutes of a data collection from the light-induced crystal, at which point the crystal fractured, when using non-alternating methods, since insufficient data would be available to perform a 'light-off/light-on' comparative data analysis process. This alternating strategy also allows the effects of gradual sample decay to be corrected for much more easily than if the data had been collected on the ground-state exclusively first, since such decay occurs at the same rate in both data collections using inter-leaving data frames. Other time-dependent systematic effects can also be eradicated, particularly the effects of synchrotron beam decay if this is the X-ray source used for the experiment. One additional design feature of such an experiment that also removes systematic effects is the collection of ground and 'ground plus light-induced' data on the same detector image frame, by shifting the detector by a small known amount in between the collection of data from each of the two states. Systematic errors such as varying signal-to-noise ratios between frames are therefore avoided. Such an approach has been demonstrated successfully using image-plate detectors.[12] However, such a method is only suitable where there are not so many diffracted spots present on the image that a detector shift is not possible without reflections from one of these images overlapping with some of those from the second image.

Irrespective of the type of pseudo-steady-state monochromatic single-crystal X-ray diffraction experiment undertaken, the necessity to fire the laser onto the sample at different crystal orientations, owing to the required goniometer angular movement for each data frame, can cause anisotropic sample photo-conversion. This is because a laser beam is inherently polarised. Unless one wishes to exploit this polarisation in some way, it is generally considered best to detune the polarisation to create an incident laser beam with circularly polarised light. In a steady-state experiment, polarisation effects do not generally cause a problem since they can be averted by either optically-pumping a stationary crystal between data collections or, as is common practice, continuously rotating the sample during the optical-pumping period.

The ms photo-active lifetime lower limit of the sample for pseudo-steady-state experiments is dictated primarily by the maximum repetition rates of pulses available in most commercial lasers, these being typically of the order of kHz. Such repetition rates derive from diode lasers, and lasers are, in fact, more commonly pumped by flash-lamps which typically operate at a 10 Hz repetition rate.

Below the ms photo-active lifetime-regime, one must collect data in a stroboscopic pump–probe manner where each frame of data derives from the integration of a number of pump–probe excitations. Note that this is distinct from the stroboscopic pump–probe pseudo-steady-state experimental methodology just described, since each frame of data in that case emanated from a single continuous X-ray (probe) exposure of the pseudo-steady-state being captured by the (pump) laser over the period of data acquisition.

A pulsed X-ray source is therefore required to study all light-driven processes with sub-ms photo-active lifetime. If one is to realise the structural perturbations that result from the technologically important high-speed electrical and optical

properties described in section 2, one needs an experimental methodology that will provide access to ms–ps lived structures.

3.3 Pulsed X-rays *via* a mechanical chopper

For samples with photo-active lifetimes in the ms–µs time regime, a mechanical chopper can be used to afford X-ray pulses. The length of each X-ray pulse is engineered to be in accordance with the photo-active lifetime of the sample. A chopper that operates a rotating wheel comprising slits of varying width radially will permit these different time-lengths (see Fig. 6). To access the widest possible range of X-ray pulse
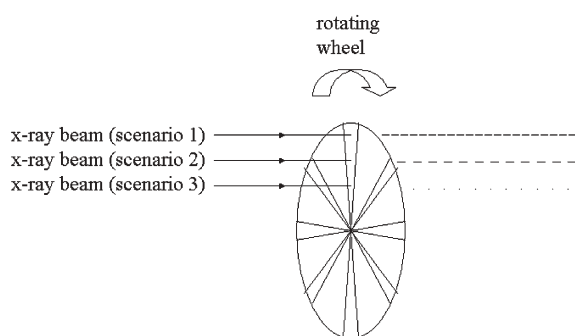
Fig. 6 A schematic diagram of a mechanical chopper used to create pulses of X-rays of varying widths, according to the position of the chopper relative to the incoming X-ray beam. The chopper axle is moved upwards or downwards to afford the different pulse widths. Three alternative options are illustrated.

lengths, this wheel will be removable from the chopper axle such that one of several wheels, each with different ranges of slit apertures, can be chosen for a given experiment. An example of one such chopper design is given by Ozawa *et al.*[13] The repetition rate of the X-ray pulses is then matched with that of the pulsed laser and the timing of the opening of the chopper is synchronised to the shutter opening of the laser such that both the optical and X-ray pulses are either 'on' or 'off' at a given instant (see Fig. 5). This way, the 'on' periods correspond to the structure of the $X\%$ photo-converted state combined with that of the $100\text{-}X\%$ non-photo-absorbed ground-state, whilst the 'off' periods relate to the fully-recovered ground-state. Each frame of data thus acquires Bragg intensity exclusively from the 'on' periods; during the 'off' periods only background is accrued. The preclusion of any contamination of Bragg intensity due to the exclusive ground-state structure avoids heavy dilution of the contrast that is sought between the ground and light-induced structure. Such contamination would present an insurmountable problem. A significant amount of dead time is introduced by this experimental methodology. Consequently, whilst a laboratory X-ray source may be used for many steady-state experiments (although, the greater flux of synchrotron radiation would always provide better contrast) synchrotron radiation is mandatory for these types of experiments where X-ray pulses are created—the several orders of magnitude greater X-ray flux available at a synchrotron is needed to compensate for the highly-depleted time-averaged flux (low 'duty-cycle') caused by pulsing the X-rays.

In terms of data collection strategies, interleaving the data frames for the exclusive ground-state and 'ground plus light-induced' data sets is very important when employing this methodology, for reasons akin to those described for the pseudo-steady-state pump–probe methodology, and because such a process also allows the implementation of time-delay strategies which minimise heating problems. Unlike in pseudo-steady-state experiments, the pulsed nature of the X-rays in

these experiments affords the freedom to off-set the laser and X-ray pulses from each other in time. This means, for example, that an additional reference data-set can be collected in an interleaved fashion, along with the collection of the ground and light-activated data sets, which will resemble the ground-state which has been affected by laser heating but not laser excitation. This is engineered by off-setting the timing of the laser and X-ray pulses such that data is not collected (X-ray shutter is not opened) until the light-induced structure has had time to relax back to its ground-state, but before it has had chance to dissipate laser heating effects. Exploiting off-sets in laser and X-ray synchronisation can also be useful in other ways. For example, one can use it for time-slicing the light-induced state to allow one to follow the evolution of a light-induced state, by observing changes in Bragg intensities of selected peaks.

The measurement and analysis of the data then proceeds in the same manner as that described for the stroboscopic pseudo-steady-state experiments with the exception of where the percentage of photo-conversion in a sample is small. Since the duty-cycle is low when pulsed X-rays are used, one has to collect a frame of data for a considerable time in order to afford Bragg peaks with adequate intensities. This contrasts with a steady-state experiment where one generally has the luxury of collecting data with very good statistics since, here, the detector read-out time, rather than data collection speed, is the time-limiting factor of an experiment. Consequently, owing to practical time constraints, one usually has to compromise the accuracy of the Bragg intensities in order to perform an experiment, that utilises X-ray pulses, over a realistic time-frame. Such a compromise most affects the viability of observing the results sought where the percentage of photo-conversion is small. In these cases, it is considered better to analyse the *difference* between two intensities collected in rapid succession, as this will yield more accurate results than the parent intensities themselves due to the avoidance of various systematic effects. This has been found in similar crystallographic difference experiments where the differences sought are similarly small.[14] In such cases, the reflection intensities are derived from the response ratio, η, according to:

$$\eta_{hkl} = \frac{I_{\text{on}}(hkl) - I_{\text{off}}(hkl)}{I_{\text{off}}(hkl)} = \frac{I_{\text{on}}(hkl)}{I_{\text{off}}(hkl)} - 1$$

where I_{on} is the intensity of the light-activated state and I_{off} represents the Bragg intensity associated with the conventional ground-state structure factor. The response ratios can be refined by least-squares methods using derivative expressions of η.[13]

3.4 Pulsed X-rays *via* the temporal structure of a synchrotron

For samples with µs–ps photo-active lifetimes, the temporal structure of a synchrotron is exploited in order to realise matching µs–ps X-ray pulses. This temporal structure derives from the fact that the electrons that are accelerated around a synchrotron ring (before being agitated magnetically to emit X-rays) do so in discreet bunches. The 'bunch width' is described in terms of the time that the full length of an electron bunch takes to pass a given point in the synchrotron and this is of the order of ns–ps. Accelerator physics can be used to harness these bunches individually to provide pulsed X-rays of a ns–ps timescale or they can be grouped together with other bunches to create a train of X-ray pulses of, in principle, any timescale up to the limiting orbit speed of the synchrotron (of the order of µs) which would correspond to the head of this train of pulses joining its own tail in the synchrotron circuit. Thus, X-ray pulses of a µs–ps timescale are available. In practice, however, there are certain restrictions on the exact timescales available since a synchrotron operates in one out of

a small selection of 'bunch-modes', since the X-ray source serves a whole variety of instruments at any one time, some of which do not require such time-structure but, in contrast, necessitate as high an X-ray intensity (thus high duty-cycle) as possible. Certain bunch modes are therefore available in a synchrotron at different times during the year. As an illustration, Fig. 7 shows the bunch modes available at the ESRF,
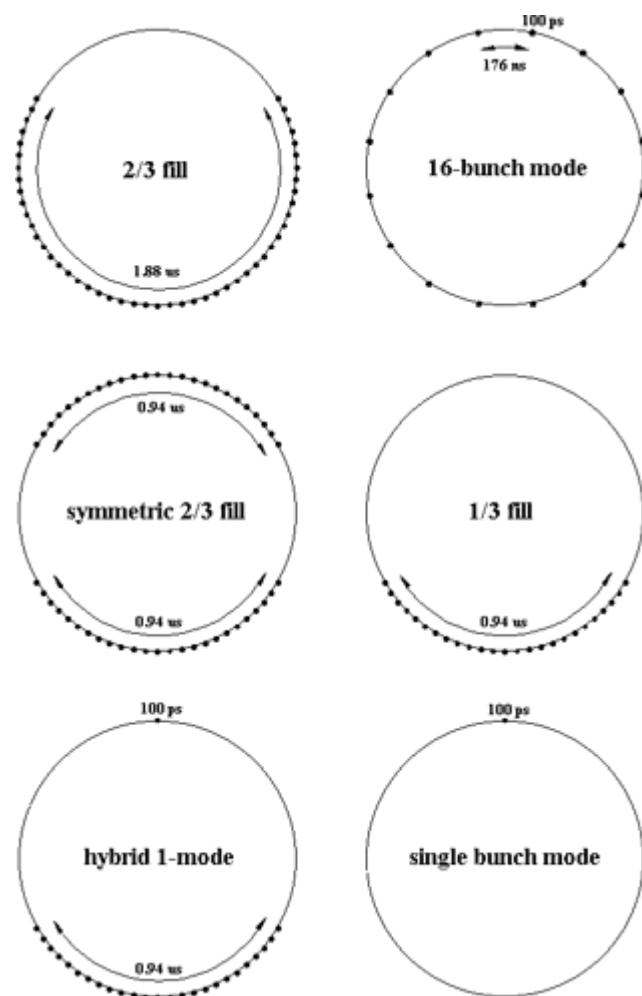

Fig. 7 The various time-structures available in the synchrotron at the ESRF, Grenoble, France.

Grenoble, France. Consequently, intermediate chopping measures may be put in place at the instrument to select out certain bunches to fine-tune the X-ray pulse time-frame to that desired for a given experiment. One such chopper, used on the ID9 beamline at the ESRF, is described by Bourgeois et al.[15]

In order to utilise the pump–probe methodology for such experiments, a ns, ps or fs pulse-width laser can be used, any of which are commercially available, together with high-speed electronics such that the required time-gated synchronisation between X-ray and laser pulses for the experiment is achieved.

The much shorter X-ray pulses, used in these experiments, result in such a low duty-cycle that obtaining sufficient X-ray flux is challenging even at the most powerful synchrotrons. Indeed, it was only eight years ago that the first results achieving ns time-resolution were published, which is nearly two decades since the first feasibility studies of the technique were carried out. The first attempt at time-gating a synchrotron X-ray pulse to a laser pulse was in fact conducted in 1980–1 using EXAFS experimentation.[16] However, all attempts failed

primarily due to beam accelerator instabilities. A reinvestigation of this methodology in 1984 led to success in the ms timescale, again employing EXAFS techniques.[17] However, it has required the significant improvements in synchrotron technology made over the these two decades to enable these ideas to be rejuvenated with success and applied to diffraction, and even now there are only a handful of publications of such results arising from ns time-resolved crystallography of photo-active species (see Section 5). Most of these studies have comprised the characterisation of transient biological species on the ns timescale and have utilised Laue diffraction techniques (from Bragg's Law: varying λ, fixed θ) rather than monochromatic oscillatory-based methods (varying θ, fixed λ), which are the principal subject of the review presented here. Laue diffraction has the huge advantage of very fast data acquisition time, since the Bragg condition is met many times simultaneously when λ is the variable parameter, as illustrated in Fig. 8.

Whilst oscillatory methods afford data much more slowly than Laue diffraction, they have the intrinsic advantage over Laue diffraction that they preclude the overlap of reflections, since one can assume that the Bragg condition is met only once at a given time in monochromatic X-ray diffraction experiments. Consequently, there is no need to deconvolve reflections that commonly hampers the resolution of the data in Laue diffraction, where reflection overlap is prevalent on account of the Bragg condition being met many times simultaneously. Since the light-induced chemical changes in these experiments are generally on a molecular scale and are often subtle, high atomic resolution is a prerequisite, thus making Laue diffraction problematic. In the aforementioned biological studies, distinct areas of electron-density, which appear in Fourier difference maps, upon creation of the transient species were revealed rather than individual perturbations on the atomic scale. In addition, instrumentally, Laue diffraction requires a 'white-beam' of X-rays that comprise a continuous range of X-ray wavelengths acting on the sample simultaneously. Instrumentally, all Laue-based experiments are therefore restricted to synchrotron sources. Big strides in the development of Laue-based X-ray crystallography have, however, been made during recent years[18] and one can probably look forward to an exciting time ahead in this regard. Furthermore, Laue diffraction is presently the only viable method to use in experiments where the crystals die very quickly upon photo-activation.

4 Complimentary laser spectroscopy measurements

Thus far, we have primarily considered only the X-ray requirements for these experiments. Entirely underpinning the diffraction experiments, however, is a vast amount of laser spectroscopy data, which should be a mandatory prerequisite for any diffraction experiment on light-activated species. Without this one is unable to decide if the sample is indeed viable for such an experiment, and if it is, this spectroscopic data is necessary so that one can be informed about the required laser and X-ray conditions for the diffraction experiment.

The photophysical properties of a compound are generally very sensitive to the sample phase, and therefore it is absolutely crucial that the parameters used to match and optimise X-ray diffraction characteristics on photo-active species derive from crystalline sample based measurements, where at all possible. Therefore, before any such X-ray diffraction experiment is carried out, each sample candidate should be screened by conducting appropriate laser experiments in order to establish the spectroscopic parameters associated with the nature of the photo-active structure sought. This screening process will typically comprise a series of laser experiments, each providing
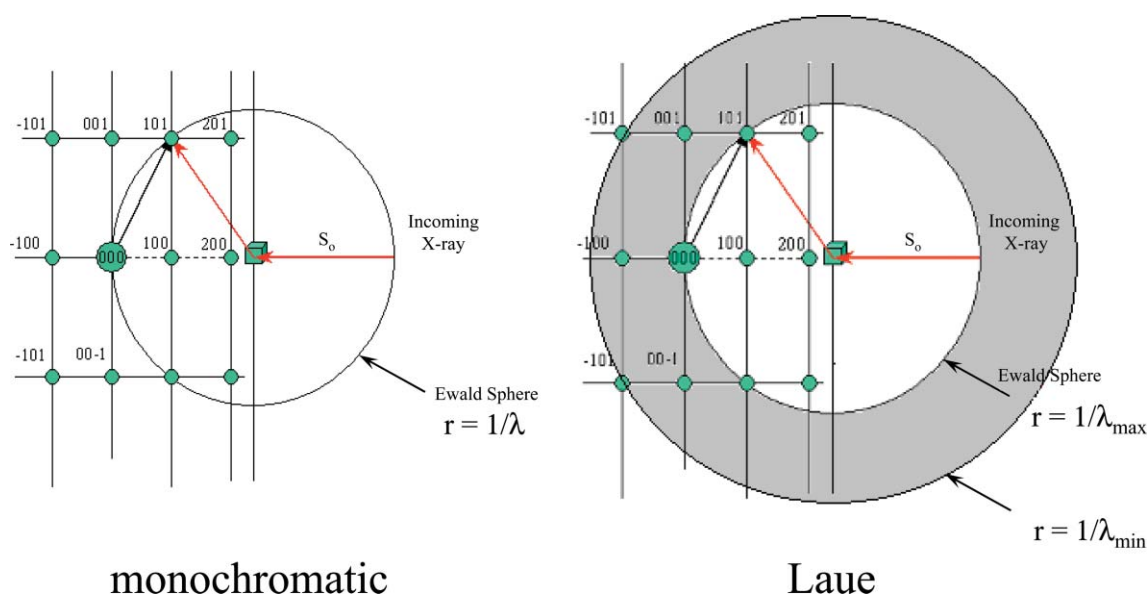
monochromatic   Laue

Fig. 8 The Ewald sphere construction for monochromatic and Laue diffraction (shown in two-dimensions). In the monochromatic case, the (rotating) reciprocal lattice shown generates a diffracted X-ray beam when a lattice point intercepts the surface of the sphere (with radius = $1/\lambda$). Only one lattice point generally intercepts this surface at any one time when using monochromatic radiation [reflection (101) in the case illustrated]. In Laue diffraction, the range of wavelengths available affords a spherical torus (with minimum and maximum radii of $1/\lambda_{max}$ and $1/\lambda_{min}$, respectively) wherein the diffraction condition is met. Consequently, a number of reflections lie in the wavelength band (shaded in grey) and so, in Laue diffraction, many reflections satisfy the Bragg condition simultaneously.

important *a priori* information for the subsequent X-ray diffraction experiments:

(i) *The UV–vis absorption spectrum in both ground and photoexcited states.* In order to calculate accurately the optical penetration depth of a laser through a single-crystal, UV–vis absorbance spectra must be recorded in both the ground and photo-activated states, at a known sample concentration, c, such that the extinction coefficient, ε, can be calculated in each case:

$1/\mu = 1/\varepsilon c$ where $1/\mu$ is the optical penetration depth (μ = absorption coefficient)

Regarding sample concentration, c, solid-state measurements would be preferable to solution-based data, where possible, particularly to avoid solvent effects. Whilst experimentally more difficult, UV–vis measurements, taken whilst the compound is in its photo-activated state are also important since the absorbance of the photo-activated state may differ from that of the ground-state, thence effecting a different optical penetration depth.

(ii) *The time-resolved emission spectrum of the compound in the solid-state at various excitation wavelengths.* This will show which wavelength range should be utilised to achieve maximum possible photo-conversion and the appropriate timing window for observation of this photo-induced state independent of other possible states.

(iii) *The lifetime of the photo-induced state measured in the crystalline phase, at the temperature at which the X-ray diffraction experiment is to be carried out.* This needs to be known exactly, since the choice of X-ray diffraction experimental methodology derives entirely from the lifetime of the sample. Solid-state requirements are very important since solvent effects can alter radically the photo-active lifetime of a sample. The temperature aspects are similarly important. Decreasing the temperature, for example, can cause the onset of quantum-mechanical stabilisation of the photo-induced state. In more extreme cases, increasing or decreasing the sample temperature can effect a complete change in the structural nature of the dominant emissive state, *e.g.* in a luminescent material which commonly converts from metal-to-ligand to intra-ligand charge transfer by a decrease in

temperature. From a purely crystallographic point of view, the temperature should be as low as possible, in order to minimise thermal effects, since libration effects may occlude structural perturbations owing to the photo-induced state. Consequently, a compromise sometimes has to be made between laser experiments and crystallographic ideals and, in any case, conventional laboratory-based X-ray diffraction should be carried out at various temperatures, as part of the testing prior to a photo-induced X-ray diffraction study, in order to assess the ground-state structure including any libration effects.

(iv) *Laser ablation studies as a function of the laser wavelength, output power, repetition rate, and the crystal size.* To ensure that the crystal can withstand laser irradiation at least for the anticipated duration of the X-ray diffraction experiment, a laser is fired at a crystal sample for a series of known durations. The laser parameters used are also systematically varied such that one can find the optimum laser conditions that will provide the greatest photo-conversion possible in the X-ray diffraction experiment without destroying the crystal.

(v) *The quantum yield at the proposed wavelength of laser excitation in the X-ray diffraction experiment.* This parameter provides a quantifiable measure of the population level of the photo-converted state that is independent of that obtained through the structural refinement against the X-ray diffraction data.

In practice, not all of the laser tests listed herein are viable with available resources, feasible preparatory timescales, or due to physical or instrumental restrictions. However, at least the basics of the tests (i)–(iv) described above are mandatory in some form since the X-ray diffraction parameters derive directly from these measurements. For a comprehensive description of laser spectroscopy experiments, one is referred to Lakowicz.[19]

5 Structural results obtained so far

The chronology of instrumental developments in this area of chemical crystallography has reflected directly the relative levels of these experimental challenges, the structure of

metastable photo-induced states being first realised in 1991[20] whilst the first report of a time-resolved small-molecule X-ray crystallography study was published only two years ago.[21] The chemical literature is therefore somewhat skewed presently towards results on materials with long-lived photo-induced states as this section illustrates. However, with continuing developments in crystallographic instrumentation, the proportion of diffraction experiments reported on long-lived *versus* transient photo-induced molecular species is likely to even out given the myriad of important applications dependent upon ephemeral light-induced structural perturbations.

Whilst this review concerns single-crystal X-ray diffraction studies, it is pertinent to remark that the first major diffraction studies on light-induced structural changes actually came from work on glasses. Most noteworthy within this context is the extensive work on the photodarkening effects of chalcogenide glasses carried out in the 1980s.[4] These studies used steady-state methods. The EXAFS community were also on the scene earlier than crystallography, for example in biology with the EXAFS-based work on the different geminate states of myoglobin[22] and the time-resolved Pt–Pt shortening in the $[Pt(POP)_4]^{4-}$ anion (POP = pyrophosphate, $[H_2P_2O_5]^{2-}$).[23]

The first report of a crystallographic study that used steady-state photo-induced methods was the investigation of a putative light-induced structural change in sodium nitroprusside (SNP), $Na_2[Fe(CN)_5(NO)]\cdot2H_2O$, undertaken by Woike and co-workers.[20,24] Neutron diffraction was used to reveal the structures of the two metastable states, MS_I and MS_{II}, known to exist in this compound under certain conditions of light exposure (wavelength and polarisation direction) and temperature control. The structure obtained for MS_I showed small but significant changes in the Fe–N, Fe–C and N–O bonds along the *trans*-O–N–Fe–CN axis, compared with that of the ground-state, also measured. Such changes are also possibly reflected in the anisotropic displacement parameters of the oxygen and nitrogen atoms (see Table 2b in ref. 24). The structure of MS_{II} indicated more marginal Fe–N and N–O bond length perturbations within the same molecular axis. Part of the drive behind this structural study was the declared potential of SNP for optical storage device application. Given that the ground-state and two light-induced states of SNP all display different optical properties,[20] the structural characterisation of each of these states was very pertinent from a materials-centred perspective as well as being innovative in an academic sense. This structural work led Coppens and co-workers to begin X-ray diffraction studies on SNP.[25] Their studies also revealed that the MS_I state undergoes a light-induced structural perturbation along the *trans*-O–N–Fe–CN axis, although their final interpretation of the data points to Fe–NO → Fe–ON ligand photoisomerisation rather than a simple bond length change. Their structural characterisation of MS_{II} yielded a further photoisomerism corresponding to the formation of a disordered η^2-bound NO moiety ligated to the Fe ion (see Fig. 9). These results became the first in a series of pioneering X-ray diffraction studies of light-induced structural studies, these being primarily of materials undergoing
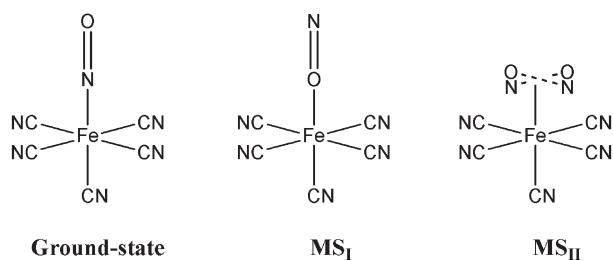
metastable ligand photoisomerism. Complexes containing η^2-N_2, NO and SO_2-based ligands were the photo-active focus of this work, as described further in their comprehensive review on ligand photoisomerisation.[26] Such studies have been stipulated to have potential for application to sunscreens and relevance to the understanding of mechanisms in certain NO and N_2-based biological processes.

In parallel with this work, photoisomerism studies have also been pursued by Ohashi and co-workers. Here, the impetus behind the work has been photo-reaction and mechanistic enquiry of reaction intermediates. Single-crystal X-ray diffraction studies have centred around analysing crystalline-state photo-reactions before and after *hv* irradiation, and have involved proton transfer,[27] heterocycle ring formation,[28] asymmetry generation and chiral inversion,[29] and radical pair formation.[30] Many such photo-reactions have been shown to be reversible upon heating, although this much depends on the level of conformational change afforded in the photo-reaction, which is often very substantial: if the change is too large, crystal fracture will occur since the crystal lattice can only withstand molecular movement up to a certain level before losing its integrity.

As an integral part of these studies, the structural manifestations of some of these conformational changes have afforded very useful insights into the topological nature of the reaction cavity site in a given series of reaction types. In some cobaloxime complexes, one of Ohashi's most featured series of compounds, the nature of reaction cavities has been further probed by photoismerism studies of cobaloxime complexes as guests within a series of cyclohexylamine hosts.[31] Coppens and co-workers have also been synthesising host–guest complexes where the guest is a photo-active species. There, the primary interest is in finding a suitable method to 'dilute' the photo-active species so that the crystal lattice is stabilised even in the case of large structural changes[32] so that one can augment the maximum percentage of excitation possible above which crystal fracture occurs.

Reaction mechanistic information has been deduced by Ohashi and co-workers in some cases and the structure of the intermediate itself has been isolated.[28] In a similar vein, the structure of photo-excited triplet states can be deduced X-ray diffraction, using stabilising cryo-trapping methods, together with supporting IR spectroscopy and theoretical calculations.[33] However, all too frequently, reaction intermediates and photo-excited states are too ephemeral to be harnessed in this fashion, but developments in time-resolved stroboscopic pump–probe X-ray diffraction methods will facilitate this goal in the future.

The evident feasibility for light-induced metastable structure determinations, hitherto described, has led to a further emerging field in photo-structural chemistry over the last few years: that concerning the characterisation of spin-cross-over transitions in magnetic materials. In 2001, Spiering and co-workers reported the first direct observation of the well-known light-induced-excited-spin-state-transition (LIESST) effect by photo-induced single-crystal X-ray diffraction.[34] The subject of this study was the complex, $[Fe(mtz)_6](BF_4)_2$, (mtz = methyltetrazole), which undergoes a photo-induced low-spin to high-spin (LS → HS) transition at low temperature, that is sufficiently stable at 10 K to collect data to determine the crystal structure corresponding to the HS state, post-irradiation ($\lambda = 514$ nm), as well as the LS crystal structure, obtained pre-photo-irradiation. The LIESST effect is evident *via* the expansion of the Fe–N bond lengths by ~0.2Å which corresponds to the $^1A_1$ (LS) → $^5T_2$ (HS) electronic transition. Complementary Mössbauer spectroscopy measurements indicate that 100% photo-conversion takes place. Other steady-state single-crystal X-ray diffraction studies have subsequently realised crystal structures of similarly photo-trapped high-spin

Fig. 9 The ground and two photo-induced metastable states of sodium nitroprusside.

state Fe-containing complexes, notably Fe(phen)$_2$(NCS)$_2$ (phen = 1,10-phenanthroline)[35] and Fe-based (pyrazol-1-yl)-pyridine derivatives.[36] Again, in these cases, changes in Fe–N bond lengths of ~ 0.2 Å afford the evidence of the spin transition.

Even more direct evidence for LIESST has been afforded by the very recent pioneering work by Gillon and co-workers. Here, single-crystal polarised neutron diffraction has been exploited to observe the LIESST effect *via* the spatial distribution of the magnetisation density in [Fe(ptz)$_6$](BF$_4$)$_2$, (ptz = 1-propyltetrazole).[37] The topological description of the magnetisation density around the iron position corresponds very well to that which one would expect from an Fe^{2+} magnetic form factor. Moreover, the magnetic moment on the iron site could be refined (to 4.05(7) μ_B) and compared with the theoretical value of the Fe^{2+} moment at saturation. Such analysis leads to a direct and quantitative measure of the percentage of photo-conversion, which, in this case, was practically 100%. The power of this technique is immense as it stands to reveal unprecedented information about photoinduced magnetic effects that is key to the understanding of their physical properties. The high potential of bistable materials for memory devices and the huge efforts presently being employed in industry to find new materials for such application further strengthens the importance of this work.

In the ms time-resolved (non-steady-state) regime, thus far, there exists results on only one complex, that pertaining to the anion, Pt$_2$(pop)$_4^{4-}$ (pop = pyrophosphate, [H$_2$P$_2$O$_5$]$^{2-}$, Fig. 10). Independently, the groups of Coppens and Ohashi
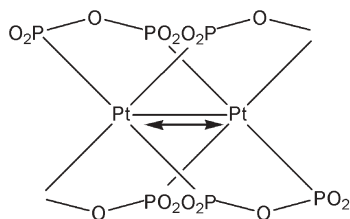

Fig. 10 The structure of the [Pt(POP)$_4$]$^{4-}$ ion. The arrow represents the Pt–Pt bond shortening that occurs upon photo-excitation.

have both deduced significant light-induced Pt–Pt bond shortening [$\Delta = -0.23$ to $-0.28(9)$ Å] in this ion by single-crystal X-ray diffraction. In each case, however, different counter-ions were used: Coppens used [(Et$_4$N)$_4$H]$^{4+}$ whilst Ohashi used [N(C$_5$H$_{11}$)$_4$]$_2$(H)$_2$. Thus, whilst the results are similar, one would expect some minor variation owing to the slightly different molecular environments surrounding the anion in the crystal lattice. The two groups also used two different experimental techniques. Coppens utilised stroboscopic pump–probe methods that exploit the aforementioned mechanical chopper design on the X3 beamline at the NSLS, Brookhaven, USA, with 50 µs time-resolution and under helium temperature.[21] Pseudo-steady-state methods were employed by Ohashi and co-workers, both in the laboratory[38] and on the BL02B1 beamline at the Spring-8 synchrotron, Japan.[12] The extent of Pt–Pt bond shortening in each case is identical within experimental error and it is also consistent with earlier results from EXAFS, electronic and optical spectroscopy measurements[23,39,40] despite the use of different counter-ions in these experiments. The results are all compatible with the rationalisation that the promotion of a Pt–Pt antibonding dσ* electron into a weakly bonding p-orbital is responsible for this structural change. The study by Coppens and co-workers shows that a concurrent 3° rotation of the Pt–Pt axis in the plane that bisects two Pt–P vectors also occurs in this photo-excitation process. Subsequent complementary density

functional theory (DFT) calculations have also been performed,[41] the results of which are consistent with the above experimental results, except that they show some discrepancy with the EXAFS results in terms of the associated Pt–P bond changes. However, this is unsurprising given the expected propensity of multiple scattering in the EXAFS spectra, that could occlude the true Pt–P distance, and the challenging nature of the DFT studies for deducing directly-bound third-row transition metal M–M excited-state bond distances.

Given the highly developmental nature of such pump–probe diffraction experiments coupled with the subtlety of the structural changes sought, obtaining consistency with analogous spectroscopic and theoretical results is very important for the quantitative assessment of the reliability of the results and thence the progression of this field. In this regard, Coppens and co-workers have recently carried out DFT calculations on a Cu(ı)bis(2,9-dimethyl-1,10-phenanthroline) ion,[42] its metal–ligand charge-transfer (MLCT) excited-state having been characterised already by Chen and co-workers,[43] using stroboscopic pump–probe EXAFS at the APS, Argonne, USA, in readiness for a second mechanical chopper based pump–probe X-ray diffraction experiment. In this EXAFS experiment, the temporal structure of the synchrotron was in fact exploited.

Diffraction studies that exploit such technology, thus making available studies of species that may be as transient as 100 ps, have mostly featured biological molecules and have thus been Laue-based in design. Whilst the subject of this review restricts itself to small-molecule single-crystal X-ray diffraction, it is pertinent to mention that there are tantalising results from this biological research sphere (see for example all references herein on work by the groups of M. Wulff and K. Moffat) and these have heavily aided technical progress in monochromatic oscillatory-based pump–probe diffraction studies at the ps–ns timescale, through the continuing improvements of the revolutionary instrument, ID9, at the ESRF, Grenoble, France, developed by Wulff and co-workers.

Consequently, several small-molecule single-crystal diffraction experiments have been conducted using the ID9 beamline, the most celebrated of which is the photo-induced paraelectric (neutral) to ferroelectric (ionic) structural phase-transition in tetrathiafulvalene-*p*-chloranil (TTF-CA).[44] Here, a 300 fs pulsed laser pump and a 100 ps X-ray probe were used to deduce the structure of its ground-state and photo-induced state, data being collected stroboscopically −2 ns and +1 ns after each laser pulse, respectively. Prior to data collection, the phase transition proceeds *via* cooperative build up of each photo-induced molecule such that there is a lead-time of ~ 500 ps required for the effect to convert from a molecular to macroscopic phenomenon. Accordingly, the evolution of the photo-induced state was monitored prior to the data collection by recording the changes in relative intensity of certain Bragg reflections over the timescale 0–500 ps. Other studies have used similar experimental set-ups to study ps–ns lived transient structures. For example, Cole and co-workers have used ID9 at the ESRF to probe the ephemeral ^{3}MLCT state of a rhenium carbene complex, [HNCH$_2$CH$_2$NHCRe(2,2′bipyridine)-(CO)$_3$]Br, which has a lifetime of ~ 230 ns.[45] Here, the feasibility of the study was confirmed in terms of experimental set-up and structural simulations. Accordingly, data were collected and initial indications from data analysis have shown that the experiment has been successful. Further data analysis is underway. Whilst this review focuses on single-crystal X-ray diffraction studies, it is pertinent to add that powder X-ray diffraction has also been used with this ps-time-resolved monochromatic oscillatory-based diffraction experimental set-up at the ID9 facility in order to deduce photo-induced structural changes in the organic molecule, *N,N*-dimethyl-amino-benzonitrile (DMABN).[46]

6 Further instrumental developments: prospects for the future

Given the very high regard for the ID9 beamline at the ESRF, there is much impetus to export this technical knowledge to create similar experimental set-ups at new synchrotron sources such as the APS and Spring-8. If such developments prevail, not only will experiments similar to those presently possible at the ESRF be possible at these sites, but one will also be able to access entirely new frontiers of time-resolved small-molecule single-crystal X-ray diffraction. At the APS, even more ephemeral light-induced structures may be probed given the shorter temporal structure of the APS synchrotron (20 ps). Spring-8 is the brightest X-ray source in the world (8 GeV) and so may be used to overcome the X-ray duty-cycle limitations that presently render certain structures elusive. The new-wave of forthcoming medium-energy synchrotrons, notably Diamond and Soleil, in the UK and France, respectively, may also afford unique opportunities for time-resolved single-crystal X-ray diffraction. In these cases, much will depend on the final specifications regarding the available electron bunch modes in the synchrotron and the single-crystal X-ray diffraction beamline specifications that will be implemented. At the Diamond facility, pump–probe time-resolved small-molecule crystallography is one of the six key areas of structural science that have been targeted for the approved single-crystal diffraction beamline.[47] Moreover, the design of this beamline has incorporated specifications for anomalous X-ray scattering (AXS) studies since this is also one of the targeted areas of structural science. AXS could be exploited very usefully in photo-induced studies in order to increase the contrast of the light-induced structure over that of the dominant ground-state, in the area of expected change within a molecule. In luminescent organometallic materials, for example, the change anticipated frequently manifests itself in a change in the M–X bond distance. A diffraction experiment could be performed readily by collecting structural data first using X-rays of a wavelength close to that of the absorption edge of this metal and then at a wavelength far from the edge. The difference between the two experiments would reveal a change in the atomic form factor explicitly due to the metal. The use of AXS in this fashion, proposed by Cole et al,[45] has yet to be exploited in practice but it stands to be a very powerful tool in analysing the commonly subtle light-induced structural changes in metal-containing compounds in the future. The beamline design at the Diamond synchrotron would be well-suited in this regard.

New technology that affords fs X-ray pulses at a synchrotron, devised by a team at the Advanced Light Source, LBNL, California,[48] may also be incorporated into the designs of one of the synchrotrons presently being constructed. Here, fs X-ray pulses are created by 'tickling' the electron beam in the linear accelerator of a synchrotron with a fs-pulsed laser in such a way that a fraction of the photons and electrons interact, resulting in photons that are scattered with regular fs-pulsed X-ray energies. Currently, proof-of-principle has been demonstrated but the resulting X-ray flux has been considered to be too weak for viable application. However, if improvements overcome this barrier, the exploitation of this technique stands to open up a whole new time-regime (ps–fs) of photo-induced X-ray diffraction studies that is presently inaccessible. The fact that chemical bond-making and bond-breaking typically occurs on the fs timescale makes such a possibility particularly exciting since one could envisage, for example, molecular movies of chemical reactions, thus revealing three-dimensional images of their mechanisms through a time-function of structural manifestations. The ability to follow phase transitions, surface processes and vibronic motion would also become possible.

Aside from synchrotrons, fs X-ray pulses will also be obtainable from Free-Electron-Lasers, and several so-called X-FEL facilities are currently planned worldwide. In Europe, the TESLA facility in Hamburg, Germany, has received much attention in this regard. The viability of fs time-resolved X-ray diffraction experiments may, however, be hampered by the fact that the X-rays resulting from an X-FEL will have far too high a flux for a crystal to survive the irradiation, although it only has to survive a few fs since it is a 'one-shot' experiment, i.e. there is no possibility for stroboscopic pump–probe experimentation as the X-rays arrive in a single flash. The 'one-shot' nature of an X-FEL also limits inherently the use of the technique for X-ray diffraction experiments, given the intrinsic requirements for reciprocal space coverage in order that a crystal structure can be afforded.

Fs-laser-induced ps-X-ray generation has also been demonstrated in the laboratory by exploiting the high spatial and spectral brightness of plasmas that, once created, emit X-ray pulses on a timescale of the order of ps and typically with a kHz repetition rate.[49,50] The development of these instrumental advances for affording laboratory-based, quantitative X-ray diffraction results would prove highly beneficial to this area of structural endeavour.

7 Concluding remarks

The excitement shared by researchers in this new area of chemical crystallography has been conveyed here, through the major technological and experimental advances and key results that have been achieved already. The huge scientific impact that small-molecule crystallography stands to deliver in studying photo-induced species has been demonstrated and one can anticipate an exciting time ahead, particularly in time-resolved stroboscopic pump–probe diffraction experiments when more results unfold from the instrumental developments, still heavily underway. The high speed at which detector technology is currently moving may yield new detectors that are more appropriate to photo-induced structural studies, especially in terms of data read-out time, background levels and sensitivity, and such advances would strongly influence continuing experimental developments across all sample lifetime regimes. One may also envisage much more advanced Laue-based methodologies for small-molecule chemical crystallography in the future and this would lead to experiments that are otherwise impossible due to rapid crystal fracture upon laser irradiation. The combined use of other facilities presently under development and the increased use of complimentary techniques such as EXAFS, powder diffraction, time-resolved infra-red and Raman spectroscopy, and density functional theory calculations, will also ease the way ahead. We have seen that complimentary laser spectroscopy provides crucial a priori information to all X-ray diffraction experiments on photo-induced species and it appears to be the continuing goal of the laser industry to provide commercial lasers that are reliable, fully-tuneable and truly 'turn-key operation', so this will aid the crystallographer enormously. However things unfold, one can be certain that the future of light-induced structure determination looks bright.

References

1　J. R. Helliwell (Ed.), *Faraday Discuss.*, 2003, **122** (Time-Resolved Chemistry: from structure to function).
2　L. X. Chen, *Angew. Chem., Int. Ed.*, 2004, **43**, 2886–2905.

3 M. Saes, F. van Mourik, W. Gawelda, M. Kaiser, M. Chergui, C. Bressler, D. Grolimund, R. Abela, T. E. Glover, P. A. Heimann, R. W. Schoenlein, S. L. Johnson, A. M. Lindenberg and R. W. Falcone, *Rev. Sci. Instruments*, 2004, **75**, 24–30 and references therein.

4 S. R. Elliott, *J. Non Cryst. Solids*, 1986, **81**, 71–98 and references therein.

5 D. Kimbrough, *J. Chem. Educ.*, 1997, **74**(1), 51–53.

6 B. Perman, V. Srajer, Z. Ren, T. Teng, C. Pradervand, T. Ursby, D. Bourgeois, F. Schotte, M. Wulff, R. Kort, K. Hellingwerf and K. Moffat, *Science*, 1998, **279**, 1946–1950.

7 S. Crosson and K. Moffat, *Plant Cell*, 2002, **14**, 1067–1075.

8 W. F. Brinkman and M. R. Pinto, *Bell Lab. Tech. J.*, 1997, 57–75.

9 O. Kahn, *Molecular Magnetism*, VCH, New York, 1993.

10 A. Y. Kovalevsky, K. A. Bagley and P. Coppens, *J. Am. Chem. Soc.*, 2002, **124**, 9241–9248.

11 A. Y. Kovalevsky, K. A. Bagley, J. M. Cole and P. Coppens, *Inorg. Chem.*, 2003, **42**, 140–147.

12 Y. Ozawa, M. Terashima, M. Mitsumi, K. Toriumi, N. Yasuda, H. Uekusa and Y. Ohashi, *Chem. Lett.*, 2003, **32**, 62–63.

13 Y. Ozawa, M. R. Pressprich and P. Coppens, *J. Appl. Cryst.*, 1998, **31**, 128–135.

14 A. Paturle, H. Graafsma, H.-S. Sheu and P. Coppens, *Phys. Rev. B*, 1991, **43**, 14683–14691.

15 D. Bourgeois, T. Ursby, M. Wulff, C. Pradervand, A. Legrand, W. Schildkamp, S. Labouré, V. Srajer, T. Y. Teng, M. Roth and K. Moffat, *J. Synchrotron Radiat.*, 1996, **3**, 65–74.

16 D. R. Sandstrom, S. C. Pyke and F. W. Lytle, *Stanford Synchrotron Radiation Lab Report 80/01 (1980) and Stanford Synchroton Radiation Lab Activities Report, April 1980 to March 1981*, 1981.

17 D. M. Mills, A. Lewis, A. Harootunian, J. Huang and B. Smith, *Science*, 1984, **223**, 811–813.

18 Z. Ren, D. Bourgeois, J. R. Helliwell, K. Moffat, V. Srajer and B. L. Stoddard, *J. Synchrotron Radiat.*, 1999, **6**, 891–917.

19 J. R. Lakowicz, *Principles of fluorescence spectroscopy*, Plenum Press, New York, 2nd edn., 1999.

20 M. Rüdlinger, J. Schefer, G. Chevrier, N. Furer, H. U. Güdel, S. Hassühl, G. Heger, P. Schweiss, T. Vogt, T. Woike and H. Zöllner, *Z. Phys. B: Condens. Matter*, 1991, **83**, 125–130.

21 C. D. Kim, S. Pillet, G. Wu, W. K. Fullagar and P. Coppens, *Acta Crystallogr. A*, 2002, **58**, 133–137.

22 L. Powers, B. Chance, M. Chance, B. Campell, J. Friedman, S. Khalid, C. Kumar, A. Naqui, K. S. Reddy and Y. Zhou, *Biochemistry*, 1987, **26**, 4785–4796 and references therein.

23 D. L. Thiel, P. Livins, E. A. Stern and A. Lewis, *Nature*, 1993, **362**, 40–43 (corrigendum: *363*, 565).

24 M. Rüdlinger, J. Schefer, T. Vogt, T. Woike, S. Haussühl and H. Zöllner, *Physica B*, 1992, **180**(181), 293–298.

25 M. D. Carducci, M. R. Pressprich and P. Coppens, *J. Am. Chem. Soc.*, 1997, **119**, 2669–2678 and references therein.

26 P. Coppens, I. Novozhilova and A. Kovalevsky, *Chem. Rev.*, 2002, **102**, 861–883.

27 T. Ohhara, J. Harada, Y. Ohashi, I. Tanaka, S. Kumazawa and N. Niimura, *Acta Crystallogr. B*, 2000, **56**, 245–253.

28 T. Takayama, M. Kawano, H. Uekusa, Y. Ohashi and T. Sugawara, *Helv. Chim. Acta*, 2003, **86**, 1352–1358.

29 A. Sekine, H. Tatsuki and Y. Ohashi, *J. Organomet. Chem.*, 1997, **536–7**, 389–398.

30 M. Kawano, Y. Ozawa, K. Matsubara, H. Imabayashi, M. Mitsumi, K. Toriumi and Y. Ohashi, *Chem. Lett.*, 2002, 1130–1131.

31 D. Hashizume and Y. Ohashi, *J. Chem. Soc., Perkin Trans. 2*, 1999, 1689–1694.

32 P. Coppens, B. Ma, O. Gerlits, Y. Zhang and P. Kulshrestha, *CrystEngComm.*, 2002, **4**, 302–309.

33 M. Kawano, K. Hirai, H. Tomioka and Y. Ohashi, *J. Am. Chem. Soc.*, 2001, **123**, 6904–6908.

34 J. Kusz, H. Spiering and P. Gütlich, *J. Appl. Cryst.*, 2001, **34**, 229–238.

35 M. Marchivie, P. Guionneau, J. A. K. Howard, G. Chastanet, J.-F. Letard, A. E. Goeta and D. Chasseau, *J. Am. Chem. Soc.*, 2002, **124**, 194.

36 J. Elhaïk, V. A. Money, S. A. Barrett, C. A. Kilner, I. Radosavljevic Evans and M. A. Halcrow, *J. Chem. Soc., Dalton Trans*, 2003, 2053–2060 and references therein.

37 A. Goujon, B. Gillon, A. Gukasov, J. Jeftic, Q. Nau, E. Codjovi and F. Varret, *Phys. Rev. B*, 2003, **67**, 220401–220404.

38 N. Yasuda, M. Kanazawa, H. Uekusa and Y. Ohashi, *Chem. Lett.*, 2002, 1132–1133.

39 W. A. Fordyce, J. G. Brummer and G. A. Crosby, *J. Am. Chem. Soc.*, 1981, **103**, 7061–7064.

40 P. Stein, M. K. Dickson and D. M. Roundhill, *J. Am. Chem. Soc.*, 1983, **105**, 3489–3494.

41 I. V. Novozhilova, A. V. Volkov and P. Coppens, *J. Am. Chem. Soc.*, 2003, **125**, 1079–1087.

42 L. X. Chen, G. B. Shaw, I. Novozhilova, T. Liu, G. Jennings, K. Attenkofer, G. J. Meyer and P. Coppens, *J. Am. Chem. Soc.*, 2003, **125**, 7022–7034.

43 L. X. Chen, G. Jennings, T. Liu, D. J. Gosztola, J. P. Hessler, D. V. Schaltrito and G. J. Meyer, *J. Am. Chem. Soc.*, 2002, **124**, 10861–10867.

44 E. Collet, M.-H. Lemée-Cailleau, M. Buron-LeCointe, H. Cailleau, M. Wulff, T. Luty, S.-Y. Koshihara, M. Meyer, L. Toupet, P. Rabiller and S. Techert, *Science*, 2003, **300**, 612–615.

45 J. M. Cole, P. R. Raithby, M. Wulff, F. Schotte, A. Plech, S. J. Teat and G. Bushnell-Wye, *Faraday Discuss.*, 2003, **122**, 119–129.

46 S. Techert, F. Schotte and M. Wulff, *Phys. Rev. Lett.*, 2001, **86**, 2030–2033.

47 W. Clegg, J. M. Cole, R. Morris, P. R. Raithby, S. J. Teat, C. C. Wilson, C. Wilson, J. Evans and M. Smith, *Diamond Light Source Technical Report*, SCI-BLP-028-0101 (www.diamond.ac.uk/Publications/1987/sci-blp-028-0101.pdf).

48 R. W. Schoenlein, W. P. Leemans, A. H. Chin, P. Volfbeyn, T. E. Glover, P. Balling, M. Zolotorev, K. J. Kim, S. Chattopadhyay and C. V. Shank, *Science*, 1996, **274**, 236–238.

49 C. Rischel, A. Rousse, I. Uschmann, P.-A. Albouy, J.-P. Geindre, P. Audebert, J.-C. Gauthier, E. Forster, J.-L. Martin and A. Antonetti, *Nature*, 1997, **390**, 490–492.

50 R. J. Tompkins, I. P. Mercer, M. Fettweis, C. J. Barnett, D. R. Klug, Lord G. Porter, I. Clark, S. Jackson, P. Matousek, A. W. Parker and M. Towrie, *Rev. Sci. Instrum.*, 1998, **69**, 3113–3117.