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**Nanosecond time-resolved crystallography of photo-induced species: case study and instrument development for high-resolution excited-state single-crystal structure determination**

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This work describes one of the first stages in the development of time-resolved photo-induced small-molecule single-crystal diffraction, whereby transient electron density perturbations, with lifetimes down to the *nanosecond* level, can be resolved at the *atomic* level. Knowledge of such ephemeral electronic effects is likely to yield key information regarding the origins of certain important physical properties, e.g. luminescent and non-linear optical effects, since it will allow the dynamics of electron density to be identified and quantified, and it is this that underpins such phenomena in a given molecule. The experimental methodology employs phase-locking pump-probe techniques such that the inherent time-structure of a synchrotron X-ray beam (nanoseconds) is harnessed and time-gated in-phase with a femtosecond laser. The resultant beams made coincident on the crystal in a periodic manner, and a diffraction pattern is recorded as a function of the Bragg angle,  $\theta$ . Such technology is based upon the pioneering work carried out in sub-nanosecond time-resolved crystallography of macromolecular

biological moieties (non-atomic resolution) at the ESRF, although one crucial difference here is the use of monochromatic irradiation and oscillatory motion rather than Laue ‘snapshot’ methodology, so that atomic resolution is possible. The experimental details of a case study conducted on ID9 at the ESRF, France, are described, whereby the feasibility of the excited-state structure determination of a luminescent rhenium carbene complex,  $[\text{HNCH}_2\text{CH}_2\text{NHCr}(\text{2,2}'\text{-bipyridine})(\text{CO})_3]\text{Br}$ , is realised. Key experimental parameters that are required for the success of such an experiment are discussed in light of this study and other feasibility work conducted at the SRS, UK, and in the laboratory. Plans, designs and tests for the implementation of this technique in the UK, first at the SRS, and thence at DIAMOND, the forthcoming UK synchrotron, are described, in particular with reference to the world-leading potential that DIAMOND could lend toward the development of this technique.

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## 1) Introduction

The photophysics of organic<sup>1</sup> and organometallic<sup>2</sup> complexes has attracted a wide level of interest over recent years on account of the very applied nature of their light emissive properties: *e.g.* for semiconductor devices, non-linear optical components and light-emitting diodes.<sup>3,4</sup> The origin of these properties lies in the nature of the excited-states of these materials, whose lifetimes typically range from  $\mu\text{s}$ -ps.<sup>2,5</sup> The photolysis process excites electrons into otherwise inaccessible states, thus inducing a redistribution of electrons that can also lead to atomic displacement within the material or more severely isomerism or solid-state chemical reactions. The effects are prevalent in organometallic species due to their low-valent metal centres and the high degree of covalency between the metal and its ligands which results in the presence of various types of low energy excited states.<sup>6</sup> The accessibility of these various states and thus the energy, intensity and lifetime of the associated light emission depends inherently on the metal type and the nature of the ligands. In principle, one could therefore tune materials to exhibit specific emissive properties by judiciously varying the metal and ligand type. However, this requires a thorough knowledge of the exact nature of excited state that is responsible for the emission. This is no

trivial matter, since this emissive state is usually a mixture of various types of low-lying excited states. One can infer a certain level of information *indirectly* through UV/vis spectroscopic measurements by comparing the different emission wavelengths, lifetimes and quantum yields for a given series of complexes and such inferences can be supported by theoretical molecular orbital-based calculations. More direct information can be obtained by recent developments in time-resolved infra-red vibrational spectroscopy.<sup>7</sup> Such work undoubtedly provides invaluable information. However, in order to be able to ascertain both *direct* and *quantitative* information regarding the excited-state structure of such materials, stroboscopic pump-probe techniques are being developed for time-resolved small-molecule single-crystal X-ray diffraction, such that photo-induced crystal structures which exist on a timescale,  $\mu\text{s}$ - $\text{ns}$  become accessible.<sup>8,9</sup> The resultant ability to build up excited-state structure / photophysical property relationships leads to the ultimate goal of being able to engineer materials with desired physical properties for a given photonic application. Whilst this paper concentrates on organometallic complexes, on account of the case study, the majority of arguments and results expressed herein also pertain equally well to organic materials where, for example, photo-induced charge-transfer processes give rise to non-linear optical effects. One of the great assets of organic non-linear optical materials over their inorganic counterparts is their fast optical response times (typically ns-ps). Therefore, analogous studies of the excited-state structure of such organic materials using the technique described herein are also underway.

Given that the changes in electronic and/or atomic configuration of the excited-state of a molecule, relative to its ground-state, can be subtle and/or localised, for example, primarily between one metal-to-ligand interaction, obtaining excited-state crystal structures at the highest possible atomic resolution is paramount in observing these changes. In terms of nanosecond time-resolved X-ray diffraction studies to date, the pioneering work has been reported on macromolecular biological moieties (non-atomic resolution) using the instrument, ID9, at the ESRF.<sup>10-12</sup> These studies use the Laue ‘snapshot’ methodology owing to the delicate nature of their samples with respect to an intense X-ray and laser beam and because atomic resolution is not usually possible and/or required to observe the biologically important conformational changes ensuing. Such bio-structural studies have proven to be very successful

and the coming of age of the Laue method in this respect is described by Ren et al,<sup>13</sup> including a survey of ten successful Laue time-resolved bio-structural studies. Corresponding software for recording and processing Laue data has also been well developed.<sup>14</sup> However, whilst the Laue method exploits the use of the entire ‘white’ X-ray beam, its coverage of the Ewald sphere can be patchy and there is significant wavelength overlap of reflections. The resolution of the resulting structure is significantly compromised as a result, relative to an analogous experiment where monochromatic irradiation and oscillatory scans as a function of the Bragg angle,  $\theta$ , are used. Given the more stringent resolution requirements for small-molecule excited-state crystallography, the feasibility of conducting a nanosecond time-resolved pump-probe experiment on ID9 using the oscillatory scanning method in tandem with the time-gating to a femtosecond laser was investigated. A perspective of this technical route has been described previously by Coppens.<sup>8</sup> The subject study is a luminescent rhenium carbene complex,  $[\text{HNCH}_2\text{CH}_2\text{NHCr}(\text{2,2'}$ -bipyridine) $(\text{CO})_3]\text{Br}$ .<sup>15</sup> Experimental details are described herein and key experimental parameters relating to the sample are discussed. Related preliminary feasibility tests both on Station 9.8 at the Synchrotron Radiation Source (SRS), Daresbury, and in the laboratory are also described. Station 9.8 is the world-leading small-molecule single-crystal synchrotron facility and these tests form the first stages of a pilot project to develop time-resolved pump-probe X-ray diffraction in the UK. The more major developments will take place on Station 9.8. Whilst the SRS is scheduled to see its demise by the end of the decade, the methodology herein proposed is being designed, taking into account the construction specifications of the new synchrotron source, DIAMOND, as they unfold. In this way, the technology developed will be readily transferable together with the instrumentation when DIAMOND comes on-line in ~5 years time.

## 2 ) Experimental

### *Structure Simulations*

A set of single-crystal X-ray diffraction data was obtained on a suitable crystal of  $[\text{HNCH}_2\text{CH}_2\text{NHCr}(\text{2,2'}$ -bipyridine) $(\text{CO})_3]\text{Br}$ , using a Bruker-Nonius Kappa CCD diffractometer, molybdenum  $K_\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ), with the crystal cooled to 150 K, using an Oxford

Cryostream crystal cooling device. The co-ordinates reported by Xue *et. al.* <sup>15</sup> were used as a starting model for the structure which was refined successfully using SHELXL-97 <sup>16</sup>. The structure of the rhenium carbene cation is shown in Fig. 1 along with an indication of the direction that the Re→C(carbene) vector,  $x$ , is expected to shift upon photo-excitation as a result of metal-ligand charge transfer (MLCT).

Following crystal structure refinement, a set of  $F_c^2$  values for all the unique data was computed and these were used as the ground state values in simulations to determine which reflections are most likely to be affected by the expected lengthening of the Re=C(carbene) double bond upon excitation to the excited state. The magnitude and direction of the Re-C vector for the ground state were computed (Re=C 2.153(4) Å), and then the co-ordinates of the carbene ligand recomputed when this ligand was moved away from the Re atom, along the Re-C vector, in successive steps of 0.01 Å between 0.01 and 0.1 Å, and in steps of 0.02 Å for increases between 0.1 and 0.4 Å [using the MOVE instruction in SHELXL-97]. For each of these 25 sets of co-ordinates (all non-metal atoms not in the carbene group were assumed to retain their ground state co-ordinates) a set of  $F_c^2$  values for all the unique data were calculated using SHELXL-97. The  $F_c^2$  dataset relating to an increase in the Re-C vector of 0.1 Å was compared with the  $F_c^2$  dataset for the ground state structure. 0.1 Å is the expected level of change in bond-length upon excitation since the ‘formal’ double bond character of the Re=C bond is reduced, Re-C single bonds being of the order of 0.1 – 0.2 Å longer than Re=C double bonds. A wide variety of changes in reflection intensity were observed for all Miller indices. It should be remembered that all these calculations are based on a 100% conversion of the structure to the excited state.

<Fig. 1 about here>

#### *The X-ray Diffraction Experiment*

The pump-probe time-resolved single-crystal X-ray diffraction experiment was performed on beamline ID9, at the ESRF, Grenoble, France. The X-rays emanate from the synchrotron via a low-K undulator

with a 20 mm period. This produces a polychromatic spectrum with only one harmonic at 16.45 keV ( $\lambda = 0.7537 \text{ \AA}$ ). The polychromatic beam was monochromated using a Si(111) double crystal monochromator and the beam was focused onto the sample in a 0.25 mm diameter spot. The average flux was  $3 \times 10^7$  photons/sec. The inherent X-ray pulse length was 110 ps after injection at 90 mA and reduced to 90 ps at the end of a fill (full width half maximum). Sub-nanosecond X-ray time-resolution was achieved by using the 16-bunch mode of the synchrotron, which has a bunch spacing of 176 ns; a chopper on the beamline running at 896.6 Hz with a vertical tunnel aperture of 0.145 mm, defines an opening time of 280 ns. One bunch is selected exclusively by centring it in this window relative to its neighbouring bunches.

A mode-locked Ti: sapphire femtosecond laser was synchronised to the radio frequency of the synchrotron in order to achieve pump-probe X-ray diffraction. The 800 nm fundamental wavelength of the laser beam, operating at a repetition rate of 896.6 Hz, was frequency doubled, lending a  $\lambda=400\text{nm}$  laser beam of 50 $\mu\text{J}$  which was focused onto the sample in a 0.25 mm diameter spot, and made coincident to match the cross-section of the X-ray beam.

A crystal sample with dimensions 60 x 50 x 40  $\mu\text{m}$  was mounted onto the  $\phi$ -axis of the diffractometer and cooled to 77 K, using an Oxford Cryosystems Cryostream cooling device and data were collected using a MAR-CCD detector. Three data sets were collected with the crystal maintained at 77K, corresponding to (i) a 'reference' ground-state structure determination - no laser irradiation (dataset **1**); (ii) a ground-state structure determination, incorporating laser heating effects by imposing a -10ns time-delay of the X-ray pulse with respect to the laser pulse (dataset **2**); (iii) the excited-state structure determination, where the laser and X-ray beams are synchronised, using a time-delay of +0.5ns (dataset **3**). These time delays between the X-ray and laser were achieved by delaying the 88.05 MHz reference pulse train that controls the synchronisation of the femtosecond optical cavity. The delay can be shifted between -1.11 ms to 1.11 ms. For the 'reference' ground state structure determination, data were collected in frames as the crystal was rotated about the  $\phi$ -axis, through 251 $^\circ$ , in 2 $^\circ$  steps, but with 1 $^\circ$  of

overlap, in each case the exposure time per frame being 13 seconds. These details were replicated for the other two data collections, except that in these cases, data were recorded through the full  $\phi$ -rotation of  $360^\circ$ .

### 3) Results and Discussion

#### *1) Case Study at the ESRF*

The focus of the work presented here is a feasibility study for the structure determination of the rhenium-carbene organometallic complex  $[\text{HNCH}_2\text{CH}_2\text{NHCre}(2,2'\text{-bipyridine})(\text{CO})_3]\text{Br}$  while under synchronised laser irradiation, so that a percentage of the molecules within the crystal are promoted into an excited state and maintained there by irradiation from a femtosecond laser. This complex was chosen for the study because it is luminescent, with the origin of the emission being assigned to a  $^3\text{MLCT}$  state. A combination of detailed UV/vis spectroscopic studies and theoretical calculations indicates that the emission is  $^3[\text{d}(\text{Re}) \rightarrow \pi^*(\text{diimine})]$ , with the latter exhibiting partial  $\sigma^*$  parentage. This indicates that in the excited state the double bond character of the rhenium-carbene bond should be reduced, and that the expected increase in Re-C should be of the order  $0.05 - 0.20 \text{ \AA}$ . Although the lifetime of this excited state is only 230 ns, in dichloromethane, at room temperature, this difference should be observable in the solid state using nanosecond time-resolved pump-probed photocrystallographic methods combined with oscillatory-based data collection. Under the experimental conditions, it should be born in mind that up to a maximum of  $\sim 20\%$  of the molecules can be typically excited at any one time without crystal fracture resulting. Thus the experiment affords the combined excited and ground state structure of the given compound. By first measuring the ground-state with a  $-10\text{ns}$  time-delay between the laser and the X-ray pulse such that all photo-excitation has decayed before each subsequent X-ray measurement, and then collecting analogous data but with the X-ray and laser pulses synchronised to a time-delay of  $+0.5\text{ns}$ , to ensure laser-excitation before X-ray exposure, the electronic perturbations of the excited-state can be obtained exclusively by taking the difference between the two experimental sets of electron density distributions. This type of time-resolved pump-probe experiment that uses the time structure of

synchrotron radiation is only required for compounds with sub-microsecond lifetimes. For materials with longer lifetimes, a mechanical chopper can be used to create a suitable X-ray pulse time-resolution with the chopper being synchronised to the laser,<sup>17</sup> and for samples with *metastable* excited states *steady state* methods can be used.<sup>8, 18-21</sup>

When considering the optimum conditions for data collection for time-resolved photocrystallographic experiments, a large number of factors have to be taken into consideration. The complex  $[\text{HNCH}_2\text{CH}_2\text{NHCr}(\text{2,2}'\text{-bipyridine})(\text{CO})_3]\text{Br}$  was selected for a number of reasons in addition to the expected significant change in one bond length and the lifetime of the excited state being in the sub-microsecond range. The complex readily affords good quality single crystals, and the crystal system is orthorhombic which is relatively high for common organometallic complexes. This level of crystal symmetry is, in fact, crucial for experiments run on beamline ID9, at the ESRF, because the instrument is optimised for 'cutting edge' time resolved macromolecular crystallography and so the sample rotation allows only one degree of freedom, thus restricting data collection to the equatorial plane. With the capability of rotation about only one axis it is not possible to obtain complete coverage of the unique part of reciprocal space in samples that crystallize in lower crystal systems, and thus the high resolution required for this type of detailed analysis is compromised. With the beamline in its present configuration, this crystal symmetry restriction can only be overcome by either removing the crystal mid-data collection and mounting it at a different orientation or by using a goniometer head fitted with tilting stages or with a suitable external attachment and changing the crystal orientation mid-data collection. Both of these alternative methods compromise significantly the resolution, since the merging of the data from different tilted orientations contains systematic errors owing to manual crystal recentring and/or angular definition of any imposed tilt – the sphere of confusion about the crystal is simply not small enough. The use of compounds that crystallize in high symmetry crystal systems is also generally very helpful, and sometimes critical, to the success of this type of experiment since the intense lasing conditions imposed upon the sample commonly cause crystal decay - the higher the inherent crystal symmetry, the fewer are the number of unique data that have to be collected for a given size of problem, and so the faster the

collection of a full unique data set. In favourable cases, where the crystal survives long enough to collect all unique data, multiple equivalent reflections that can be used for data averaging and scaling can also be readily obtained.

The wavelength of laser radiation chosen is also crucial to the success of the experiment. While the laser must provide enough energy to produce enough excited state molecules to be detected, the radiation must not be absorbed so strongly that a high enough proportion of the energy is converted to heat and the crystal destroyed. Laser wavelengths at or close to absorption maxima should generally be avoided as this will lead to all the photons within the laser pulse being absorbed within the first few microns depth of the crystal. In this experiment with  $[\text{HNCH}_2\text{CH}_2\text{NHCr}(\text{2,2}'\text{-bipyridine})(\text{CO})_3]\text{Br}$ , the laser wavelength used was 400 nm whereas the absorption maxima occur at 365, 318 and 273 nm, in dichloromethane at room temperature, and an emission maximum lies at 565 nm. Related to the wavelength of the laser is the size of the crystal and with it the associated optical penetration depth. For the molecule studied here, the crystal contains *ca.*  $1.9 \times 10^{21}$  molecules per  $\text{cm}^3$ . Given a lasing energy of  $50\mu\text{J}$  at  $\lambda=400\text{nm}$ , there are approximately  $1 \times 10^{14}$  photons per laser pulse. Calculations using the Beer-Lambert law, assuming an absorption cross section of  $5 \times 10^{-17}$  per molecule, shows that >99% of the photons should be absorbed in less than 1 micron of the crystal. This equates to only a fraction of a percent of the total number of molecules within the crystal being excited. However, experiments on several different sized crystals, all using the laser in the same configuration as that used for the primary experiment reported herein, indicate that this value is largely underestimated – the laser was fired at eight crystals ranging from 40-100 $\mu\text{m}$  diameter in the direction of the laser beam path. Laser ablation was observed in all crystals where the laser path through the crystal exceeded 50 $\mu\text{m}$ . An example of the laser damage on one such crystal (90  $\mu\text{m}$  diameter in laser beam path) is shown in Fig. 2(a) and (b): as the laser cannot pass entirely through the crystal, local heating effects at the maximum point of optical penetration becoming extreme and the crystal is gradually ‘eaten away’ by the laser over a period of several minutes. Both crystals tried with either 40 or 50  $\mu\text{m}$  diameters in the laser beam path direction did not suffer any observable crystal

damage, and were stable in the laser beam over several hours of irradiation. Fig. 2(c), (d) and (e) show the crystal ultimately used for this experiment before, during, and after laser irradiation, respectively. Moreover, sustained laser irradiation of a 50  $\mu\text{m}$  diameter crystal rendered a noticeable photochemical colour change (turning orange) of the formerly yellow sample throughout the bulk of the crystal, thus indicating optical penetration greater than 50  $\mu\text{m}$ . The calculations based on the Beer-Lambert law rely intrinsically on the value of the extinction coefficient. This parameter is normally measured using solution state UV/vis spectroscopy, at room temperature, as in this case study and in general, solid-state spectroscopic data is rarely available for compounds of interest. A sharpening of the absorption bands is observed typically when comparing solution state spectroscopic measurements with analogous solid-state spectra and lowering the temperature stands to alter considerably not only the width of this band but also its general profile since the accessibility of excited-states toward absorption from the ground state will vary according to energy. However, even by bearing in mind these assumptions, thereby calculating the optical penetration depth with large tolerances for the extinction coefficient, only values much lower than 50  $\mu\text{m}$  were obtained. This suggests that whilst these calculations are very useful as a guide, they may not represent fully the optical effects on the crystal bulk, perhaps due to the influence of competing multi-photon processes and/or temporal optical changes in the environment local to a ground-state molecule that neighbours one or several in its excited state, for example.

<Fig. 2 about here>

As the determination of the excited state structure relies on the accurate measurement of small differences in intensities between the ground and excited state data collections, it is necessary to maximise atomic scattering power and definition of the atomic coordinates for each part of the experiment. For this reason the crystal was cooled to 77 K as this enhances the definition and intensity of the diffraction data by reducing the level of thermal motion within it. In addition, lowering the temperature generally enhances the lifetime of the excited state as shown in this case by UV/vis spectroscopy taken at room temperature and 77K (as a glass)<sup>15</sup> Thus excited-state data can be captured with a greater population inversion than will otherwise be possible, when the operating limits of the time-

resolution of the pump-probe instrumentation are comparable to the excited-state lifetime of the crystal, thus enhancing the contrast between ground and excited state structures. Indeed, for materials with particularly short lifetimes, lowering the temperature will make possible photocrystallography of some compounds that are otherwise impossible at the room temperature.

All data reduction and initial processing were carried out using the MOSFLM suite of programs,<sup>22</sup> which are usually used for processing macromolecular data. Details of the three data collections including the number of reflections measured, the level of reflection redundancy, and the merging  $R$  factor for equivalent reflections are presented in Table 1. A notable feature of the data is the 32-fold redundancy of total reflections measured to unique reflections in data sets **2** and **3**. The corresponding  $R_{\text{merge}}$  values are also relatively low. Since the software parameters for integration in MOSFLM are optimised for macromolecular crystallographic structure determination, non-standard settings need to be used for small molecule crystallographic data. The full optimisation of the parameters for small-molecule data processing is currently in progress<sup>23</sup> and it is anticipated that the statistics given, whilst already favourable, will improve in the final processing. In addition, accurate absorption correction procedures are being tested out. A good absorption correction is particularly important for this compound, as it will be in most organometallics of interest for pump-probe photocrystallography, since not only are heavy atoms present in the structure, but also the photoinduced structural changes expected pertain principally to the local metal environment, owing to the dominant triplet MLCT character of the excited-state. Therefore, care must be taken to ensure that structural changes observed in this area can be distinguished from possible artifacts relating to X-ray absorption effects. Full details of the data analysis and structure refinement for the compound used in the case study will be presented in a future publication.

*<Table 1 about here>*

In the experiments described above, over 100,000 reflection data may be recorded. Since the expected differences in reflection intensities between ground and excited state may be small and there are many reflections to compare, it has been found helpful to augment the diffraction experiments with additional information. Simulation studies that indicate which reflections in a data set may be subjected to the

greatest change in magnitude if the predicted structural changes occur upon excitation can prove very useful in this respect. Since, in the case of  $[\text{HNCH}_2\text{CH}_2\text{NHCr}(2,2'\text{-bipyridine})(\text{CO})_3]\text{Br}$ , spectroscopic data and theoretical calculations indicate that the rhenium carbene bond will lengthen upon excitation, and as a consequence the diimine ligand will move further away from the rhenium along the  $\text{Re}\rightarrow\text{C}(\text{carbene})$  vector, a series of simulations, as described in previous section, were performed. In addition to identifying the reflections affected most by this structural change, consistent with the reduction in ‘formal’ bond order, the simulations were also used to establish the minimum bond length change that might show significant differences in the intensity data. Five strong reflections whose  $F_c^2$  values changed between 15-80% upon excitation were selected from the unique data. The variation in the  $F_c^2$  value of these reflections, (0, 0, 10), (3, 3, 8), (10, 2, 7), (4, 12, 9) and (4, 0, 2), as a function of increasing Re-C distance was determined (see Fig. 3). The reflections all follow a non-linear variation in the range 0.01 – 0.4 Å, the (10, 2, 7) and the (4, 12, 9) reflections being the most sensitive to distance. Given that the error in experimentally determined intensities for all reflections in the dataset varies by a considerable amount, the estimated standard deviation associated with each photoinduced intensity perturbation must be calculated for individual reflections. Such uncertainties were computed for the five selected reflections by assuming the same percentage error of a structure factor whether derived from theory or experiment. An inspection of the level of these uncertainties, shown in Fig. 3 (the estimated standard uncertainties are all less than 4%), indicates that intensity changes corresponding to greater than 0.02Å increases of the Re–C bond length will be observable if excited-state conversion were 100%. Clearly, as has been stated previously, only a maximum of 20% conversion is likely to occur without crystal degradation and so the calculated differences must be scaled down to account for this incomplete conversion. It may be possible to determine the exact percentage conversion for a particular sample from spectroscopic studies and then a scale factor could be included in the calculation.

<Fig. 3 about here>

*II) Plans, designs and feasibility studies for the development of photocrystallography in the UK*

ID9 at the ESRF is truly world-leading in terms of pump-probe time-resolved X-ray diffraction and has far-reaching applications, including photocrystallography as shown above. However, it is formally a beamline for macromolecular crystallography and thus is understandably optimized for Laue experiments. Moreover, its unique ability to realize time-resolved data on sub-nanosecond photo-induced processes puts it in very high demand for experiments requiring 100ps-ns time-structure. Therefore, whilst experiments focusing on longer-lived processes ( $\mu\text{s}$  or greater) can be carried out on the beamline, the availability of alternative instrumentation that could use a mechanical chopper to obtain the required time-structure from a multi-bunch synchrotron beam for such work would optimize resources in this rapidly growing area of research. The requirements for X-ray flux are also much less demanding for microsecond time-resolved studies and so a medium energy synchrotron would be well suited for such developments. Such developments using chopper design are already underway in the USA but European access to these resources will be inevitably restricted. The current developments for the new UK synchrotron, DIAMOND, due to come on-line in 2006, would make the building of such a beamline here an optimal choice for Europe since, in addition, to the possibility of designing the instrument from scratch and optimising it for time-resolved studies, it will provide a unique opportunity to tailor the type of insertion device to such studies, and characteristics that are more fundamental to the synchrotron ring could also be considered pending similar demand from other proposed beamlines, since many of the exact specifications of the synchrotron are still fluid at this stage.

Station 9.8, at the SRS, the current UK synchrotron, is world-leading in its capacity as a single-crystal diffraction synchrotron facility, and so the exploitation of the leading instrumentation and expertise in this remit, that is readily transferable to DIAMOND, provides strong additional scientific reason to the UK being the proposed site for these developments in Europe. Developing time-resolved diffraction on a dedicated single-crystal diffraction beamline will also make it highly desirable for the study of more transient species, that possess crystal symmetry lower than orthorhombic (approximately 75% of all reported crystal structures are either triclinic or monoclinic, as deduced from a statistical search in the

Cambridge Structural Database, Version 5.23, April 2002<sup>24</sup>) since this is problematic on ID9 in its present configuration, if high atomic resolution is to be realised, as stated earlier. Given the availability of a high enough brilliance off an insertion device on DIAMOND, and a suitable bunch mode of the synchrotron, the realization of ps-ns time-resolved photocrystallography on DIAMOND is eminently possible and would offer excellent complementarity to studies at the ESRF. Developing time-resolved photocrystallography at a medium energy synchrotron, where the inherent temporal structure of the synchrotron is used, also means that even shorter-lived photo-induced structures than those that are presently possible can be captured - the lower energy characteristics of such a synchrotron compared to those of a high energy synchrotron, such as the ESRF, result in less electron-electron repulsion such that shorter bunches are possible. The ESRF, for example, has a 100ps bunch width, whilst if the tentative specifications of DIAMOND are met, a bunch width of 10-30ps will be realized.<sup>25</sup> Given the enormous range of important photonic processes that occur on the picosecond time-scale, let alone other photo-induced phenomena, the ability to study photocrystallography in the time regime, 10-100ps, would allow a myriad of new structural science to be studied. The direct and quantitative acquisition of three-dimensional structural information at this time-scale would also be highly complementary to recent advances in time-resolved spectroscopy at the picosecond level.

Technical designs for the development of a single-crystal diffraction beamline on DIAMOND that will encompass photocrystallography are currently underway. A 2 Tesla multipole wiggler is proposed as the insertion device. This will suit well the proposed photon energy range of 5-65 keV which will be directed to the instrument *via* a plane bent collimating mirror and a fixed exit sagittal focusing monochromator, and optimized for 5-40 keV by a following plane bent focusing mirror. This energy range would allow the contrast sought between ground and excited-state data in photocrystallography measurements to be maximised by the exploitation of wavelength tuneability: depending on the chemical nature of the target compound, atomic scattering factors may be enhanced by conducting experiments at longer wavelengths compared with 16 keV at which most conventional single-crystal experiments are carried out, whilst shorter wavelengths would be optimal in cases where absorption is high. The possibility of collecting

data at shorter wavelengths is particularly pertinent for the study of the type of organometallic materials highlighted in this paper since the dominant structural differences expected lie close to a heavy metal and care must therefore be taken to discern between real structural differences and artifacts due to residual X-ray absorption effects. Moreover, the energy range proposed for this instrument would inherently allow the contrast local to the metal environment in the excited-state to be increased by using anomalous X-ray scattering techniques: 5-65 keV will allow access to the absorption K-edges for Vanadium to Ytterbium and absorption L-edges from Cesium to the end of the periodic table. A multipole wiggler is the best option to cope with the requirements of wavelength precision and selectivity over the dynamic range proposed. In order to realize an X-ray time-structure, a double-wheel rotating chopper system and associated time-gating equipment has been designed to produce X-ray pulses of lengths tunable down to 1-10  $\mu\text{s}$ .<sup>26</sup> The proposed instrument has been designed to be able to accommodate ancilliary equipment for achieving the more technically demanding ps-ns time-structure. A full feasibility study will be conducted as soon as the relevant design specifications of DIAMOND unfold to assess the viability of using this time structure. One of the crucial specifications in this regard is the type of bunch modes that will be available. The option that may suit all parties is a hybrid structure where a multibunch component lies at the opposite side of the  $\mu\text{s}$  orbit to a single-bunch. In this case, the rotating chopper mentioned above could be readily adapted to time-gate out the single bunch from the rest of the beam whilst other beamlines not needing the temporal resolution of the synchrotron could continue to receive high flux during this time. The diffractometer itself will comprise a three-circle goniometer and possess a helium open-flow cryostream for operating at temperatures down to about 30K. Several detectors are envisaged so as to cover the maximum solid-angle possible per unit time. However, since CCD detector technology is advancing so rapidly at the moment, these specifications will be designed at a later stage. A reliable incident beam monitor will also be important to ensure optimal data normalization, given the small differences sought in these experiments and a fluorescence detector will be added to quantify that arising from the crystal. The type of laser remains unspecified since this technology is also rapidly advancing at the moment but a laser encompassing a widely tunable wavelength is envisaged.

Feasibility testing for photocrystallography has recently begun using Station 9.8 the SRS, where it is planned to run a pilot-project to start developing this technology, keeping in mind the technical specifications of DIAMOND as they unfold such that the technology developed at the SRS will be readily transferable to the new UK synchrotron. In a commissioning period, the viability of the instrumental set-up for this technique on Station 9.8 was assessed. A suitable instrument set up together with a laser and an Oxford Cryostream Helix apparatus, capable of cooling crystals to 26K, was realised and tests showed that it could readily be used to study crystalline materials with excited state lifetimes in the micro to millisecond range. In parallel to these tests, the feasibility of steady state excited state structure determinations has been also been investigated in the laboratory, at the University of Bath, using a Bruker Nonius Kappa CCD diffractometer, which is equipped with a sealed-tube X-ray source, together with a 10Hz Continuum 8010 seeded Nd:YAG pump laser (6-7 ns pulse width) with ND6000 dye laser component, borrowed from the Central Laser Facility Laser Loan Pool, UK. Complementary laboratory studies are crucial to the optimisation of key experimental parameters for the synchrotron based work. Similar steady-state laboratory studies in the UK have also been shown to yield long-lived excited-state crystal structures of technological importance.<sup>21</sup>

#### 4) Conclusions

A feasibility study on nanosecond time-resolved single crystal X-ray diffraction *via* the oscillation method, carried out on ID9 at the ESRF, has been shown to be successful. Key experimental parameters relating to the sample have been identified. In particular, considerations of the optical penetration depth through a crystal at a given wavelength, temperature and X-ray absorption effects, and the effects of crystal symmetry on data collection methodology are paramount to the success of an experiment. In addition, simulations have shown that the level of atomic resolution that can be obtained is sample specific and in the case study is sensitive enough to the subtle changes expected. Data collection methodologies and means by which intensity differences upon excitation can be accessed and optimised have been identified. An outlook for developing photocrystallography in the UK is described and associated technical design specifications and initial feasibility tests are outlined. If the potential

proposed herein can be harnessed, time-resolved photocrystallography stands to become an important new area of structural research, not only for photonics as the discussion is restricted to here, but it is equally applicable to scientific endeavours in areas such as photoisomerisation studies, solid-state reactions, spin cross-over transitions in magnetic materials, and understanding electroluminescent and triboluminescent phenomena.

#### Acknowledgements

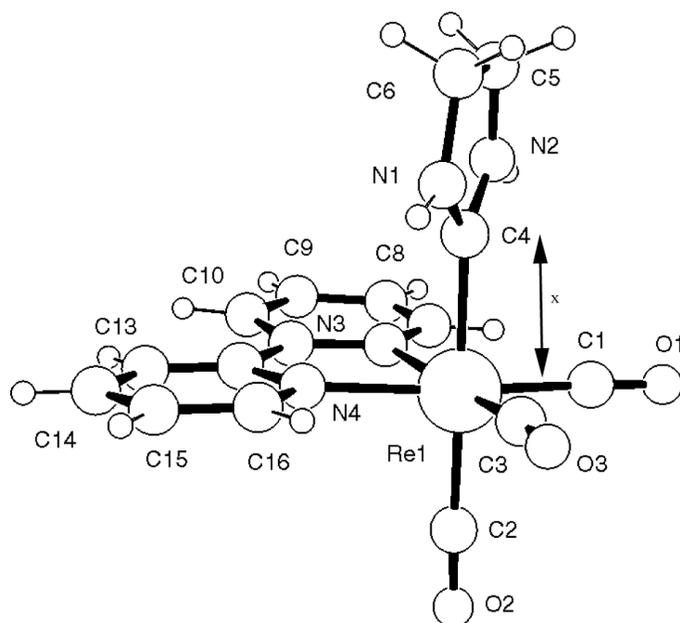
The authors wish to thank the Central Laser Facility (CLF) for laser loan pool (Mike Towrie and Sue Tavender) for preliminary experiments; Tony Parker and Pavel Matousek at the CLF for valuable discussions; Harry Powell at the Laboratory of Molecular Biology, MRC, Cambridge, for assistance with MOSFLM analysis; SRS for use of commissioning time on Station 9.8 for feasibility testing; ESRF for access to synchrotron beamtime and facilities; St. Catharine's College, Cambridge, for a Bibby Research Fellowship (JMC) and the Royal Society for a University Research Fellowship (JMC).

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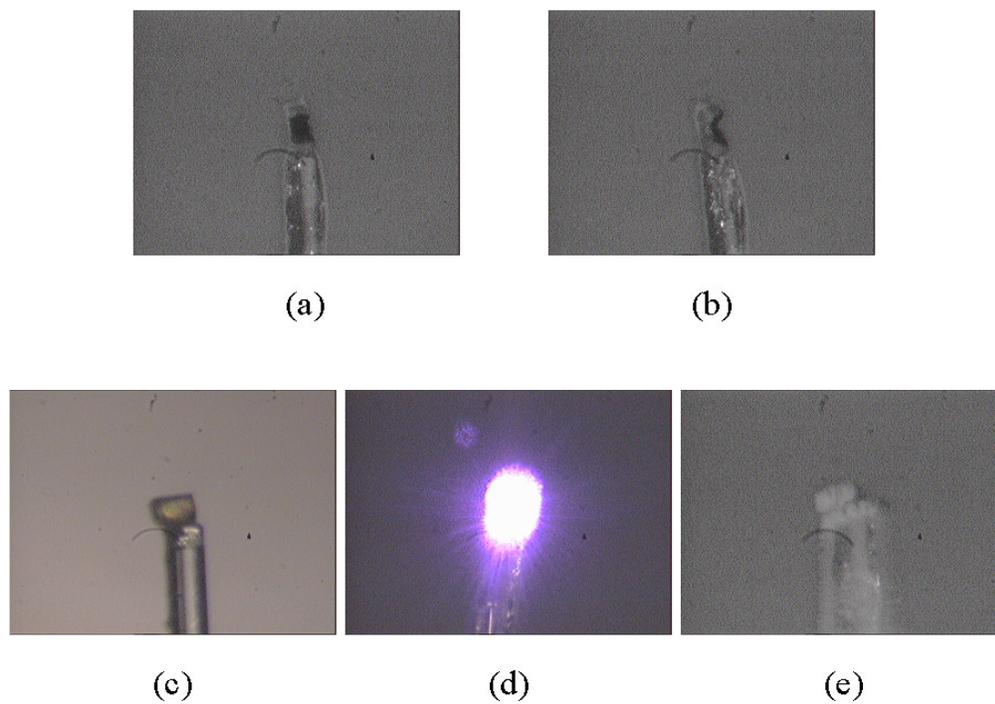
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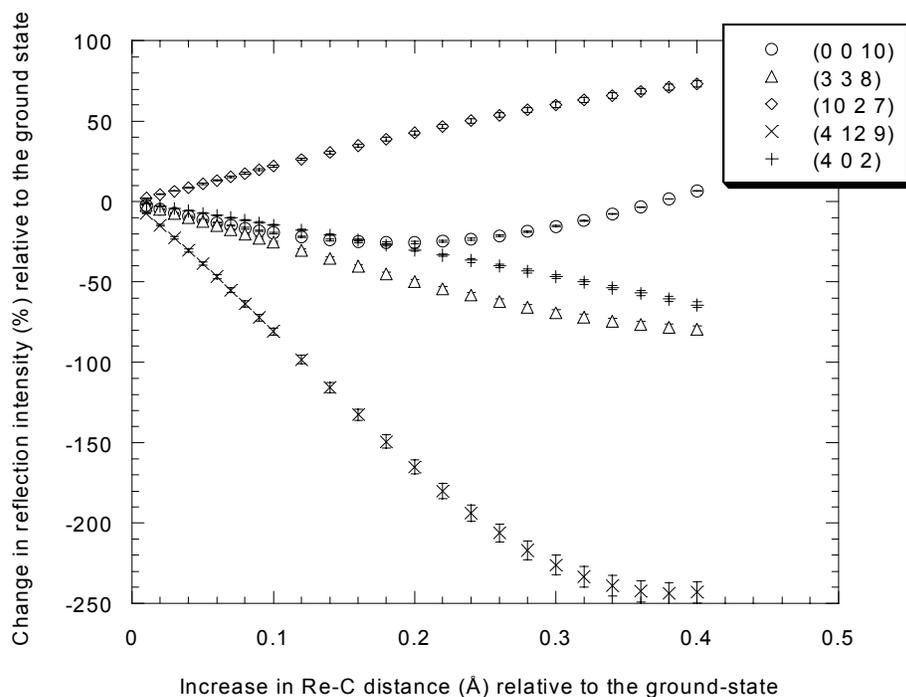
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**Fig. 1.** The structure of the  $[\text{HNCH}_2\text{CH}_2\text{NHCr}(2,2'\text{-bipyridine})(\text{CO})_3]^+$  cation showing the direction of the displacement of the diimine carbene ligand used to compute the simulated  $F_c^2$  values.



**Fig. 2** Crystals of  $[\text{HNCH}_2\text{CH}_2\text{NHCre}(2,2'\text{-bipyridine})(\text{CO})_3]\text{Br}$  mounted on a glass fibre and centred on the phi-axis of ID9 at the ESRF and subjected to a laser beam of  $\lambda = 400 \text{ nm}$  at  $50 \mu\text{J}$ . Photos (a) and (b) are different views of a crystal of  $90 \mu\text{m}$  diameter in the laser beam direction post-irradiation; photos (c), (d) and (e) relate to  $40 \times 50 \times 60 \mu\text{m}$  crystal ultimately used in the case study before, during, and after laser irradiation, respectively. Note that the view of the crystal in (e) is slightly obscured by ice that formed around the crystal during the experiment. Only amorphous contributions due to the icing were observed in the diffraction patterns.



**Fig. 3** A plot of the percentage change in intensity of five selected reflections as the Re-C(carbene) bond length is increased in the simulated structures.

**Table 1.** Data Reduction and Integration Statistics for datasets **1**, **2** and **3**.

Data	No. full reflns	No. partial reflns	Total no. obs refln	Total no.unique reflns	No. Outliers rejected	No. reflns measured only once	No. observed reflns	$R_{\text{merge}}$ all reflns
<b>1</b>	51512	13909	81560	3241	288	176	3714	0.064
<b>2</b>	79993	19314	120096	3729	581	8	3729	0.100
<b>3</b>	79411	19295	119719	3730	791	10	3729	0.090