

Structural studies of light-induced excited states

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Over the past few years there has been a marked increase in the number of structural studies carried out on light-induced excited states. Until now, however, there has been no systematic approach to the irradiation of samples, which can make data collection difficult and results unreliable. This paper presents a device for mounting a laser on a CCD diffractometer; this device not only enables the collection of data without any constraints on the data collection strategy, but also simplifies alignment of the laser and can be left in place permanently.

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1. Introduction

With the increasing interest in structure–property relationships there has been an increase in the variety of sample environments available, for example, cryostats and pressure cells. In addition, the increase in the number of known materials that respond to light has led to considerable interest in studying the associated structural changes. One example of these changes is the short-lived photo-induced state of the luminescent rhenium carbene complex, $[\text{HNCH}_2\text{CH}_2\text{NHCr}(\text{2,2}'\text{-bipyridine})(\text{CO})_3]\text{Br}$ (Cole *et al.*, 2003). Similarly, irradiation can induce charge transfer (Gu *et al.*, 2001), and structural studies have been carried out on the short-lived laser-induced ferroelectric structure of tetrathiafulvalene-*p*-chloranil (Collet *et al.*, 2003).

Examples of photoswitching involving a more dramatic structural change, such as the reorganization of ligand coordination, have also been reported. Complexes where there are different coordination modes that can be switched using light include NO ligands in sodium nitroprussides (Coppens *et al.*, 1998) and SO_2 ligands in ruthenium sulfur dioxide compounds (Kovalevsky *et al.*, 2002). A further example of photo-induced structural changes is sometimes to be found in iron(II) spin-crossover complexes (Marchivie *et al.*, 2002; Money *et al.*, 2003; Niel *et al.*, 2004; Thompson *et al.*, 2004). These materials undergo structural modifications coupled with changes to the optical, magnetic and physical properties; these changes can be stimulated by temperature or pressure changes and sometimes, at low temperature, by irradiation with light [light-induced excited spin-state trapping or LIESST (Decurtins *et al.*, 1985)].

To our knowledge, the structural study of light-induced states has generally been a little haphazard, using a ‘point and fire’ approach to irradiation, where the laser is pointed at the sample and aligned by eye. There are two key problems with this method: it is not certain that the sample is being completely irradiated and it is difficult to study structures under continuous irradiation, as movements of the diffractometer circles potentially change the alignment and may lead to obstruction of the laser beam. This latter necessity, and the number of samples that we are currently working on, has led us to design a laser stand that not only enables the continuous irradiation of samples during data collection but also, because of the robust nature of the apparatus, enables it to remain *in situ* as a permanent feature

during routine experiments. Here we present the main characteristics of the apparatus that we are using to carry out structural studies on metastable light-induced states of spin-crossover complexes.

2. Design

The key aspect of the design hinges on the mounting of the laser on the detector arm, in such a way that the laser beam remains centred on the sample irrespective of movements of the diffractometer circles. The intense collimated light from the laser is directed towards the crystal using a combination of mirrors and prisms. In the case of the work carried out in Durham, the requirement was for a device that could be used to irradiate a single crystal continuously at 30 K. Thus the instrumentation initially dictated certain aspects of the design, and this device was designed for an Oxford Cryosystems HeliX mounted on a three-circle Bruker diffractometer. The nature of the HeliX means that the crystal resides inside a beryllium nozzle, so the laser must approach the sample from below. The only area that is never obstructed by the ϕ circle mount is the region in front of the detector, so the device consists of a series of mirrors and prisms mounted on a cradle attached to the front of the detector arm (Fig. 1). Since it is a necessary requirement that the laser and mirrors move together, the laser is mounted vertically on the tail of the detector arm, behind the detector, pointing down. The mass of the lasers used is relatively low (less than 0.2 kg), so they place no significant extra load on the apparatus, leading to no damage to the instrument or introduction of any systematic error. From behind the detector, the laser beam passes vertically down past the tail of the detector arm and is reflected by a tilted mirror so that it passes alongside the detector (parallel to the detector arm). The beam then travels through a periscope made from two prisms, which deflect the beam to the front of the detector, so that it is travelling along the 2θ direction. Finally, a mirror mounted in front of the detector reflects the beam up, striking the crystal from beneath, so that it avoids the beryllium nozzle from the HeliX cryostat (Fig. 2).

This laser device has been designed to fit both a Bruker SMART 1K and a Bruker APEX CCD area-detector diffractometer; however, with minor modifications, it could probably be adapted to fit almost any diffractometer. When using the older diffractometers, where the

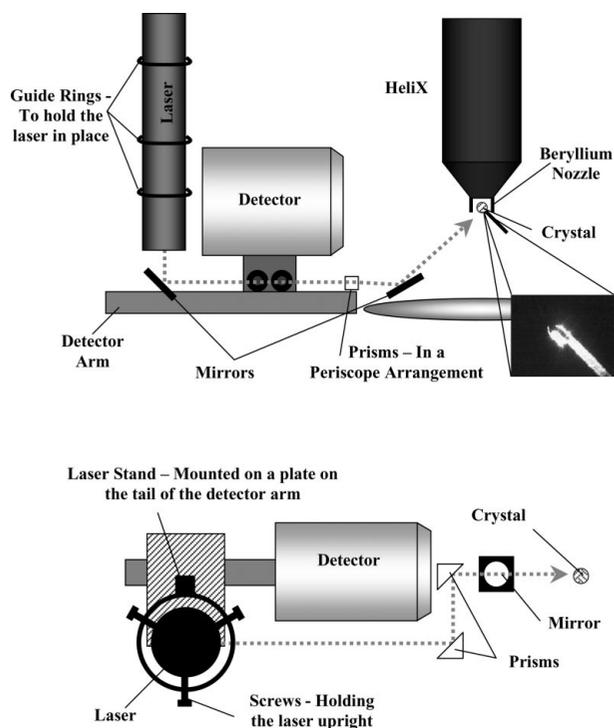


Figure 1

A schematic of the laser mounting and alignment device viewed in profile (top) and from above (bottom), with the path of the laser shown as a broken line. The laser beam travels vertically down and is reflected by a mirror, so that it travels alongside the detector arm until two prisms redirect it to the front of the detector, where a second mirror directs the beam up towards the sample. Minor adjustments to the alignment of the beam can be carried out using small screws to modify the angle of the mirrors. A photograph of a crystal on irradiation is shown inset.

crystal is viewed using a microscope, it is not possible to see the crystal during irradiation, as focused laser light can cause serious damage to the eye. However, like most modern diffractometers, the APEX is fitted with a digital camera for crystal alignment. Scattered laser light is visible using the camera and causes no damage to it, and thus can be used to facilitate accurate laser alignment.

Within the described setup, the laser can be aligned before the start of the experiment and even without a crystal. This feature increases the likelihood of success by avoiding having to perform the alignment when a precious sample is already at very low temperature and after having performed several multi-temperature data collections. In addition, the use of area detectors has reduced the data acquisition time, therefore reducing the cost of the experiment, particularly when an expensive cryogen like helium is needed to achieve the required temperatures. Coupling these improvements with the increased accuracy of the alignment as a result of the presence of the digital camera makes light-induced structural studies much more feasible.

3. Conclusion

We have presented schematics of a device designed to simplify the collection of data on light-induced excited states. This device is cheap and easy to use, and the two adjustable mirrors make it easy to align the laser should it be necessary (*e.g.* after changing the laser for one of a different wavelength). The device is also so stable and unobtrusive that we have been able to leave it in place as a permanent feature, and it is now common to carry out routine data collections with the laser mounted.

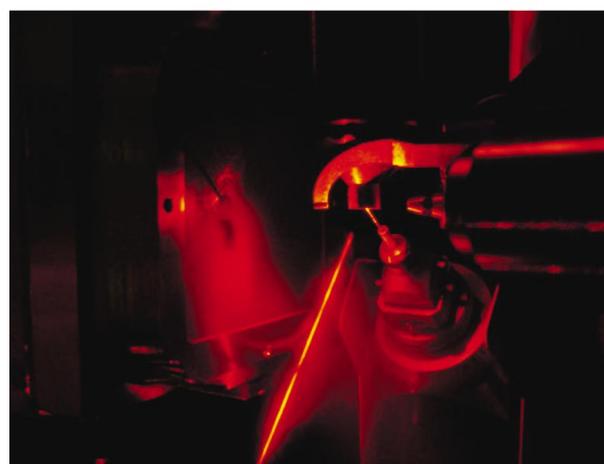


Figure 2

The laser mount and guidance system, with the laser beam path added in red (top) together with a close up of the goniometer, with the laser beam approaching the crystal from below (bottom). A 633 nm HeNe laser is shown, but 532 nm CW-Nd:YAG and 830 nm diode lasers have also been used. For these lasers the typical power at the sample is ~ 2 mW, which should lead to a temperature increase at the sample of less than 1 K, indicating that the effects seen when using this device are photophysical rather than photothermal.

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References

- Cole, J. M., Raithby, P. R., Wulff, M., Schotte, F., Plech, A., Teat, S. J. & Bushnell-Wye, G. (2003). *Faraday Discuss.* **122**, 119–129.
- Collet, E., Lemée-Cailleau, M.-H., Buron-Le Cointe, M., Cailleau, H., Wulff, M., Luty, T., Koshihara, S.-Y., Meyer, M., Toupet, L., Rabiller, P. & Techert, S. (2003). *Science*, **300**, 612–615.
- Coppens, P., Fomitchev, D. V., Carducci, M. D. & Culp, K. (1998). *J. Chem. Soc. Dalton Trans.* pp. 865–872.
- Decurtins, S., Gütllich, P., Hasselbach, K. M., Hauser, A. & Spiering, H. (1985). *Inorg. Chem.* **24**, 2174–2178.
- Gu, Z.-Z., Einaga, Y., Sato, O., Fujishima, A. & Hashimoto, K. (2001). *J. Solid State Chem.* **159**, 336–342.
- Kovalevsky, A. Yu., Bagley, K. A. & Coppens, P. (2002). *J. Am. Chem. Soc.* **124**, 9241–9248.
- Marchivie, M., Guionneau, P., Howard, J. A. K., Chastanet, G., Létard, J.-F. & Goeta, A. E. (2002). *J. Am. Chem. Soc.* **124**, 194–195.
- Money, V. A., Evans, I. R., Halcrow, M. A., Goeta, A. E. & Howard, J. A. K. (2003). *Chem. Commun.* pp. 158–159.
- Niel, V., Thompson, A. L., Goeta, A. E., Enachescu, C., Hauser, A., Galet, A., Muñoz, M. C. & Real, J. A. (2004). *J. Am. Chem. Soc.* Submitted.
- Thompson, A. L., Goeta, A. E., Real, J. A., Galet, A. & Muñoz, M. C. (2004). *Chem. Commun.* DOI:10.1039/B403179B>.