

# Photocrystallography – common or exclusive?

Katarzyna N. Jarzemska\*

Department of Chemistry, University of Warsaw, Żwirki i Wigury 101, 02-089 Warsaw, Poland. \*Correspondence e-mail: katarzyna.jarzemska@uw.edu.pl

**Keywords:** photocrystallography; commentary; best practice; synchrotron; XFELs.

Single crystals are unique, being characterized by a well-defined three-dimensional structure. This property makes them excellent model systems to mimic real-world situations, but also to supplement solution-sample studies or model the (inter-)surface environment. Therefore, it is understandable that crystallographic methods can be applied to a great number of problems from a wide range of scientific fields, including chemistry, physics, biology, medicine, materials science, geology, *etc.* In the early days of crystallography, over 100 years ago, crystal structure determination based on X-ray diffraction data constituted a challenge (Authier, 2013). The development of methods over the years and novel technical solutions opened up new opportunities not accessible before. Hence, crystallography can now be fairly easily combined with high-pressure, multi-temperature or spectroscopic research. In this way, crystallographic studies have gained additional dimensions and enabled investigations of materials behaviour under various conditions. While structural studies have become nearly routine (even including experimental charge-density investigations; Coppens, 2005), similar to high-pressure structural research, which is now conducted by a large number of scientists, photocrystallographic studies are significantly less common. This does not mean, however, that investigations of light and matter interactions are not important, but rather shows that the experiments, especially the time-resolved ones, are usually very demanding, both technically and in terms of data processing and interpretation.

Indeed, the importance of photocrystallographic studies cannot be overestimated. Interaction of light and matter is a phenomenon crucial for processes which are relevant industrially [*e.g.* solar (Grätzel, 2001, 2009) or photoelectrochemical cells (Coggins & Meyer, 2016; Alibabaei *et al.*, 2013)] or biochemically [*e.g.* light-induced biological transformations in proteins (Schmidt, 2023) or photochemical reactions of biological importance like retinene isomerization (Wald, 1968)]. Nevertheless, despite real breakthroughs towards the understanding of theoretical principles of light and matter interactions, the description of real-world systems remains a challenging task. This is due to the complexity of such systems; thus, theoretical predictions are often inaccurate or not even feasible. The common point of light-induced processes is the energy of light conversion into some other action, such as charge transfer within a molecule. This can further trigger transformations in which the molecule changes its geometry, reacts with adjacent moieties, changes its function, emits photons of a different energy, *etc.*, which may then translate into the properties of a material. Therefore, despite the great success of advanced theoretical tools, independent experimental data are needed in order to track light-induced processes occurring in molecular systems, as well as to verify the theoretical modelling methods. The understanding of light-induced processes will then contribute to our understanding of nature and shall stimulate materials design for specific applications.

Photocrystallography, with its roots in the 1950–60s, has many different faces (Coppens, 2003, 2011, 2017; Hatcher & Raithby, 2013, 2014; Cole, 2008; Jarzemska & Kamiński, 2023). It covers static methods which can be readily realised using a home laboratory diffractometer and a simple source of light. In this way, metastable products of light-induced processes can be determined. Nowadays, there are special light-delivery assemblies which facilitate uniform crystal exposure to LED/laser light *in situ* on a diffractometer (Kamiński *et al.*, 2016; Yufit, 2017; Brayshaw *et al.*, 2010). In turn, far more complex is the problem of studying very short-lived photogenerated species. A very important breakthrough came with strong X-ray sources – synchrotrons and, more recently, XFELs (X-ray free-electron lasers) – capable of producing very short X-ray



pulses of sufficient intensity (down to femtoseconds for XFELs). Equally important was the development of high-repetition and high-power lasers and advanced detectors. *Via* synchronization of laser and X-ray pulses, it became possible to track structural dynamics upon light excitation of the sample. Such studies are challenging; however, the complexity of the problem depends on the time-resolution and the sample (protein, metal–organic framework, small-molecule crystal, *etc.*) (Hatcher *et al.*, 2022; Kang *et al.*, 2024; Pandey *et al.*, 2020; Łaski *et al.*, 2024; Spence *et al.*, 2012; Ren *et al.*, 1999). Nowadays, more and more is becoming possible – data handling software is being written, new technical solutions are being applied [for some examples, see Henning *et al.* (2024), Levantino *et al.* (2021), Milne *et al.* (2017), Palmer *et al.* (2019), Yabashi *et al.* (2015, 2017), Hoshino *et al.* (2015) and Chollet *et al.* (2015)], however, time-resolved photocrystallographic studies are still rather unique and exclusive (Schmidt, 2021), especially for small molecular systems (Kang *et al.*, 2024; Hatcher *et al.*, 2022).

So as to broaden the community and encourage researchers to use the methods, review articles showing the fundamentals of the approaches, most significant examples of such studies, but also guiding the reader through various stages of sample preparation and experiment planning, are very much needed. Some previous examples include introductions to high-pressure studies (Katrusiak, 2008) or applications of charge-density methods in chemistry (Koritsanszky & Coppens, 2001). For this reason, a review work by Hatcher, Warren & Raithby (Hatcher *et al.*, 2024) on methods in molecular photocrystallography, being a part of the recently initiated *Best practice in crystallography* series in *Acta Crystallographica Section C: Structural Chemistry*, is very important. It constitutes a solid source of knowledge on how to approach the problem, how to plan one's experiment and how far one can get nowadays. The authors explain the matter from scratch and provide information on what to pay attention to. They stress the importance of complementary methods for the characterization of sample properties. The reader is given a number of examples of both static and time-resolved research, method development, problems and successes. Therefore, researchers may get a feeling of what is currently possible to achieve with their sample and, if needed, whom to ask for collaboration thanks to a well-selected bibliography.

Currently, a lot is being done at large facilities to attract a wider number of scientists and help them with regard to experiment planning, data treatment and analysis. Almost every major synchrotron is being considerably upgraded to boost its performance and provide even more unique capabilities. The recently improved sources include the European Synchrotron Radiation Facility (ESRF) in France and the Advanced Photon Source (APS) in the USA, whereas Spring-8 (Super Photon Ring – 8 GeV, Japan) and DESY (Deutsches Elektronen-Synchrotron, Germany) will be upgraded soon. Furthermore, an increased amount of and new science is being done on XFEL sources in terms of time-resolved studies of various kinds. The experiments are becoming more accurate and precise, while data collections

are much faster and automatic data treatment protocols are becoming more user-friendly. Therefore, in order to make use of the increased scientific capabilities and the financial resources invested, new users will be more than welcome.

Furthermore, due to the vast development of detectors, X-ray sources, *etc.*, it is possible to do much more in the home laboratory. This is also well described in the article by Hatcher *et al.* (2024). Being involved in one of the first in-house time-resolved photocrystallographic experiments realised in Philip Coppens' laboratory (University at Buffalo) (Trzop *et al.*, 2014; Kaminski *et al.*, 2014; Deresz *et al.*, 2021), it is great to see new technical and methodological solutions (Casaretto *et al.*, 2017) which have proven that the pulsed X-ray source is not necessarily needed and the hybrid pixel-array detector (HPAD), with its fast-gating properties, can do a great job in collecting data with millisecond time resolution (note that later a similar approach was implemented at the synchrotron as well; Hatcher *et al.*, 2022). I am sure that we will shortly see some great science out of that.

Hence, it would be a pity not to make use of these achievements if they are becoming available at hand, especially when the importance of solid-state studies, as opposed to solution, is increasing because many novel electronic devices are solid-state devices (including thin single-crystal or polycrystalline films, *etc.*) or alternatively solid-state catalysts and other materials of real-life applications. It is therefore extremely important to teach and provide the scientific community with such inspiring review articles collecting important knowledge and showing the best practices in the field. However, another aspect is to let people gain some hands-on experience and the possibility to meet experts in the field. This can be done *via* the running of various workshops, such as the IUCr High Pressure Workshops, Zürich School of Crystallography or European Crystallographic Schools (ECSs) (note that some photocrystallography topics appeared during ECSs in Nancy this year and in Warsaw in 2017). Unfortunately, in the field of photocrystallography, despite its vast development, not much has been done since the first event of this kind (Workshop on Dynamic Structural Photocrystallography in Chemistry & Materials Science) organized by Philip Coppens in 2013 in Buffalo (more than 10 years ago!) (Trzop & Jarzemska, 2013). Maybe it is high time to change that?

### Acknowledgements

KNJ thanks the National Science Centre in Poland for funding (SONATA BIS programme).

### Funding information

The following funding is acknowledged: Narodowe Centrum Nauki (grant No. 2020/38/E/ST4/00400).

### References

Alibabaei, L., Luo, H., House, R. L., Hoertz, P. G., Lopez, R. & Meyer, T. J. (2013). *J. Mater. Chem. A*, **1**, 4133–4145.

- Authier, A. (2013). In *Early Days of X-ray Crystallography*. Oxford University Press.
- Brayshaw, S. K., Knight, J. W., Raithby, P. R., Savarese, T. L., Schiffers, S., Teat, S. J., Warren, J. E. & Warren, M. R. (2010). *J. Appl. Cryst.* **43**, 337–340.
- Casaretto, N., Schaniel, D., Alle, P., Wenger, E., Parois, P., Fournier, B., Bendeif, E.-E., Palin, C. & Pillet, S. (2017). *Acta Cryst.* **B73**, 696–707.
- Chollet, M., Alonso-Mori, R., Cammarata, M., Damiani, D., Defever, J., Delor, J. T., Feng, Y., Glowina, J. M., Langton, J. B., Nelson, S., Ramsey, K., Robert, A., Sikorski, M., Song, S., Stefanescu, D., Srinivasan, V., Zhu, D., Lemke, H. T. & Fritz, D. M. (2015). *J. Synchrotron Rad.* **22**, 503–507.
- Coggins, M. K. & Meyer, T. J. (2016). *Photoelectrochemical Solar Fuel Production*, edited by S. Giménez & J. Bisquert, pp. 513–548. Switzerland: Springer.
- Cole, J. M. (2008). *Acta Cryst.* **A64**, 259–271.
- Coppens, P. (2003). *Chem. Commun.* pp. 1317–1320.
- Coppens, P. (2005). *Angew. Chem. Int. Ed.* **44**, 6810–6811.
- Coppens, P. (2011). *J. Phys. Chem. Lett.* **2**, 616–621.
- Coppens, P. (2017). *Struct. Dyn.* **4**, 032102.
- Deresz, K. A., Łaski, P., Kamiński, R. & Jarzemska, K. N. (2021). *Crystals*, **11**, 1345.
- Grätzel, M. (2001). *Nature*, **414**, 338–344.
- Grätzel, M. (2009). *Acc. Chem. Res.* **42**, 1788–1798.
- Hatcher, L. E. & Raithby, P. R. (2013). *Acta Cryst.* **C69**, 1448–1456.
- Hatcher, L. E. & Raithby, P. R. (2014). *Coord. Chem. Rev.* **277–278**, 69–79.
- Hatcher, L. E., Warren, M. R. & Raithby, P. R. (2024). *Acta Cryst.* **C80**, 585–600.
- Hatcher, L. E., Warren, M. R., Skelton, J. M., Pallipurath, A. R., Saunders, L. K., Allan, D. R., Hathaway, P., Crevatin, G., Omar, D., Williams, B. H., Coulson, B. A., Wilson, C. C. & Raithby, P. R. (2022). *Commun. Chem.* **5**, 102.
- Henning, R. W., Kosheleva, I., Šrajer, V., Kim, I.-S., Zoellner, E. & Ranganathan, R. (2024). *Struct. Dyn.* **11**, 014301.
- Hoshino, M., Adachi, S. & Koshihara, S. (2015). *CrystEngComm*, **17**, 8786–8795.
- Jarzemska, K. N. & Kamiński, R. (2023). *Comprehensive Inorganic Chemistry III (Third Edition)*, edited by J. Reedijk & K. R. Poepelmeier, pp. 273–310. Oxford: Elsevier.
- Kaminski, R., Benedict, J., Trzop, E., Jarzemska, K., Fournier, B. & Coppens, P. (2014). *Acta Cryst.* **A70**, C775.
- Kamiński, R., Jarzemska, K. N., Kutyla, S. E. & Kamiński, M. (2016). *J. Appl. Cryst.* **49**, 1383–1387.
- Kang, J., Lee, Y., Lee, S., Ki, H., Kim, J., Gu, J., Cha, Y., Heo, J., Lee, K. W., Kim, S. O., Park, J., Park, S.-Y., Kim, S., Ma, R., Eom, I., Kim, M., Kim, J., Lee, J. H. & Ihee, H. (2024). *Nat. Chem.* **16**, 693–699.
- Katrusiak, A. (2008). *Acta Cryst.* **A64**, 135–148.
- Koritsanszky, T. S. & Coppens, P. (2001). *Chem. Rev.* **101**, 1583–1628.
- Łaski, P., Bosman, L., Drapała, J., Kamiński, R., Szarejko, D., Borowski, P., Roodt, A., Henning, R., Brink, A. & Jarzemska, K. N. (2024). *J. Phys. Chem. Lett.* In the press. <https://doi.org/10.1021/acs.jpcllett.4c02476>.
- Levantino, M., Kong, Q., Cammarata, M., Khakhulin, D., Schotte, F., Anfinrud, P., Kabanova, V., Ihee, H., Plech, A., Bratos, S. & Wulff, M. (2021). *C. R. Phys.* **22**, 75–94.
- Milne, C. J., Schietinger, T., Aiba, M., Alarcon, A., Alex, J., Anghel, A., Arsov, V., Beard, C., Beaud, P., Bettoni, S., Bopp, M., Brands, H., Brönnimann, M., Brunnenkant, I., Calvi, M., Citterio, A., Craievich, P., Csatari Divall, M., Dällenbach, M., D'Amico, M., Dax, A., Deng, Y., Dietrich, A., Dinapoli, R., Divall, E., Dordevic, S., Ebner, S., Erny, C., Fitze, H., Flechsig, U., Follath, R., Frei, F., Gärtner, F., Ganter, R., Garvey, T., Geng, Z., Gorgisyan, I., Gough, C., Hauff, A., Hauri, C. P., Hiller, N., Humar, T., Hunziker, S., Ingold, G., Ischebeck, R., Janousch, M., Juranic, P., Jurcevic, M., Kaiser, M., Kalantari, B., Kalt, R., Keil, B., Kittel, C., Knopp, G., Koprek, W., Lemke, H. T., Lippuner, T., Llorente Sancho, D., Löhl, F., Lopez-Cuenca, C., Märki, F., Marcellini, F., Marinkovic, G., Martiel, I., Menzel, R., Mozzanica, A., Nass, K., Orlandi, G. L., Ozkan Loch, C., Panepucci, E., Paraliiev, M., Patterson, B., Pedrini, B., Pedrozzi, M., Pollet, P., Pradervand, C., Prat, E., Radi, P., Raguin, J.-Y., Redford, S., Rehanek, J., Réhault, J., Reiche, S., Ringele, M., Rittmann, J., Rivkin, L., Romann, A., Ruat, M., Ruder, C., Sala, L., Schebacher, L., Schilcher, T., Schlott, V., Schmidt, T., Schmitt, B., Shi, X., Stadler, M., Stingelin, L., Sturzenegger, W., Szlachetko, J., Thattil, D., Treyer, D. M., Trisorio, A., Tron, W., Vetter, S., Vicario, C., Voulot, D., Wang, M., Zamofing, T., Zellweger, C., Zennaro, R., Zimoch, E., Abela, R., Patthey, L. & Braun, H.-H. (2017). *Appl. Sci.* **7**, 720.
- Palmer, G., Kellert, M., Wang, J., Emons, M., Wegner, U., Kane, D., Pallas, F., Jezynski, T., Venkatesan, S., Rompotis, D., Brambrink, E., Monoszlai, B., Jiang, M., Meier, J., Kruse, K., Pergament, M. & Lederer, M. J. (2019). *J. Synchrotron Rad.* **26**, 328–332.
- Pandey, S., Poudyal, I. & Malla, T. N. (2020). *Crystals*, **10**, 628.
- Ren, Z., Bourgeois, D., Helliwell, J. R., Moffat, K., Šrajer, V. & Stoddard, B. L. (1999). *J. Synchrotron Rad.* **6**, 891–917.
- Schmidt, M. (2021). *Biophys. Rev.* **13**, 1191–1197.
- Schmidt, M. (2023). *Struct. Dyn.* **10**, 010901.
- Spence, J. C. H., Weierstall, U. & Chapman, H. N. (2012). *Rep. Prog. Phys.* **75**, 102601.
- Trzop, E., Fournier, B., Jarzemska, K., Sokolow, J., Kaminski, R., Benedict, J., Chen, Y., Henning, R. & Coppens, P. (2014). *Acta Cryst.* **A70**, C776.
- Trzop, E. & Jarzemska, K. (2013). *ACA RefleXions*, **3**, 66.
- Wald, G. (1968). *Nature*, **219**, 800–807.
- Yabashi, M., Tanaka, H. & Ishikawa, T. (2015). *J. Synchrotron Rad.* **22**, 477–484.
- Yabashi, M., Tanaka, H., Tono, K. & Ishikawa, T. (2017). *Appl. Sci.* **7**, 604.
- Yufit, D. S. (2017). *J. Appl. Cryst.* **50**, 1556–1558.