Diamond-II
Proposal for flagship project
SWIFT
(Spectroscopy WithIn Fast Timescales)

Science Group: Spectroscopy

Case prepared by: **Sofia Diaz-Moreno, Giannantonio Cibin, Diego Gianolio, Veronica Celorrio, Konstantin Ignatyev, Tina Geraki, Stuart Bartlett, Sylvia Britto, Fred Mosselmans, Shu Hayama, Monica Amboage, Matteo Aramini, Luke Keenan.**

John Sutter, Optics Group Scientist

Outline proposal for a flagship beamline project Diamond-II

1. Summary/Impact statement

Taking advantage of the added capacity offered by Diamond-II, we proposed to build a new beamline to perform X-ray Absorption Spectroscopy. The new beamline, called SWIFT (Spectroscopy WithIn Fast Timescales), will be a high flux beamline optimized for the study of samples under *operando* conditions, with the added potential to investigate sample heterogeneities at the 20 µm scale. The beamline will exceed the capabilities of the other XAS beamlines in the group for experiments that require an element of time resolution in dilute samples, and will bridge the existing spatial resolution gap between I18 and B18. SWIFT will offer these new capabilities but also provide the much-needed extra capacity to our community, easing the demand on B18, systematically oversubscribed by more than a factor of 3 and amongst the three most productive physical sciences beamlines at Diamond.

The new beamline design draws on the experience gained in the Spectroscopy Group and the user community, on high flux, time- and space- resolved XAS, aiming at a highly efficient design, that will deliver state of the art spectroscopic data on evolving and heterogeneous systems.

2. Scientific Case

X-ray Absorption Spectroscopy (XAS) is a very powerful tool for the study of the electronic and local geometric structure of a specific element. The high sensitivity of the method together with its element selectivity make it possible to undertake experiments under realistic conditions of concentration, and its applicability to crystalline or amorphous solids, liquids and gases makes this method ideal for the study of processes under *operando* conditions. In the hard X-ray regime, the application of XAS techniques has the advantage that little compromise is required for integrating many complex sample environment setups, enabling applications in various scientific disciplines, from chemistry and catalysis, to environmental science, energy materials, physics, biology, medicine, and cultural heritage.

SWIFT will bring a competitive advantage to our community and will impact all research areas mentioned above. In this outline proposal, we focus on applications in Chemistry and Catalysis, and Energy Materials, the two most active communities using the spectroscopy beamlines at Diamond.

Chemistry and Catalysis.

As described in the Diamond-II Science Case, the capability of following processes under *operando* and realistic conditions of concentration, temperature and other external parameters, is essential to understand the mechanisms that govern chemical processes. This knowledge is an essential requirement for developing new strategies for materials design and synthesis. SWIFT, with its enhanced capability to follow processes on timescales of tenths of milliseconds, will make a major contribution to this scientific area.

The combination of spatial and temporal resolution is essential in the field of heterogeneous catalysis, enabling tracing the kinetics of fast reactions and the dependency on gas feed and position in the catalyst bed, in a similar manner as was demonstrated by Dann et al.[1] for a rapidly oscillating CO oxidation reaction in an industrial catalyst (3% Pd on γ-Al2O3). The higher flux available at SWIFT will enable these experiments to be performed at lower catalyst loadings using the fluorescence detection mode.

The enhanced time resolution of SWIFT will also play a key role in following the evolution of liquid mixtures in real time in the field of homogeneous catalysis. This capability is particularly useful for investigating chemical production of pharmaceuticals and fine chemicals, by enabling the characterization of distinct short-lived reaction intermediates. In addition, the sub-second resolution achieved in fluorescence detection mode will be ideally suited to follow fast crystal nucleation and nanoparticle formation and growth, where the concentrations of the components of interest are typically in the millimolar range. Reactions such as the synthesis of magnetite[2], where the thermodynamic crystallisation product is formed within 30-60 seconds, or the growth of catalytic Pd/Pt core-shell alloy nanoparticles with reaction rates on the order of seconds[3], are well suited to the time resolution capabilities offered by SWIFT.

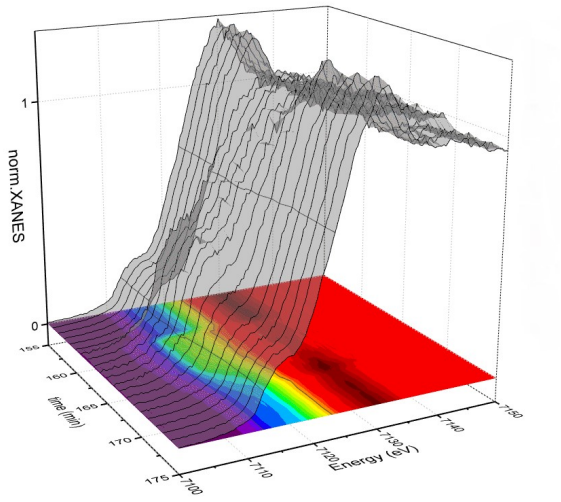

Figure 1. Evolution of the structure of an Fe-based electrocatalyst during HER conditions. The very sharp change at 160 minutes corresponds to a rapid switch between Fe(II) and Fe(0).

Measurements under modulation excitation conditions would also find significant advantages when matched with the time resolution of a fast scanning monochromator. These approaches are particularly powerful for investigating reaction mechanisms in more dilute systems. This will find applications in, for example, heterogenous catalysis, where gas feed composition is varied periodically[4], or electrochemical reactions, where the periodic voltage variations will change the concentration of a given species.

Electrocatalytic reactions, such as the example studied by Genovese et al.[5], will also profit from the fast scanning capabilities and high flux of the proposed beamline. In this study, the formation of hydride species at very negative potentials (-1.5 to -2.0V) on an iron based electrocatalyst under hydrogen evolution reaction (HER) conditions was proposed, but the authors could not probe its existence (Figure 1). SWIFT will enable these types of study on faster time scales and with an extended spectral range, so a full structural study of the processes by following the EXAFS region of the absorption spectrum can be performed.

Energy Materials.

The growing global demands for alternative energy sources to fossil fuels and the increasing awareness of environmental pollution have motivated the development of electrochemical devices that can convert green energy into electricity and store it. As highlighted in the Diamond-II case, XAS has been extensively used to advance our understanding on the structure, chemical nature and electronic state of energy materials, not only on their pristine state or after usage, but also as they evolve during a reaction or process. It is known that most of these electrochemical reactions experience sluggish reaction kinetics, so a deeper understanding of the electrocatalysts' reaction mechanism is necessary to drive improvements in system performance.

The high time resolution offered by SWIFT will deliver the capability to move beyond the study of thermodynamic steady states into the determination of transient states in electrochemical reactions. Experiments such as the example performed by Yu et al.[6] on the high rate de-lithiation behaviour in $LiFePO_4$, or the study by Fabbri et al.[7] on the reconstruction of a highly active perovskite nano-electrocatalysts for water splitting, will be accessible using SWIFT. In the field of battery research, this spectrometer will thus enable the study of materials under high-rate operating conditions, in a similar fashion to the studies by Zhou et al.[8]. Quicker acquisition times will also open the door to the investigation of reactions on time scales relevant for modern synthesis methods like hot-injection[9], microwave-assisted,

microfluidics, and supercritical flow. All these approaches are relevant in the fabrication of photovoltaic materials.

3. Benefit to the Diamond research community

Diamond must develop experimental facilities that satisfy the ever-increasing demand for *in situ* and *operando* measurements. SWIFT will offer capabilities that will increase the international competitiveness of the Diamond spectroscopy instrumentation suite and its academic and industrial user community. In particular, the proposed beamline will benefit the chemistry community, the largest user base of the Spectroscopy Group, currently responsible for more than 60% of the publications of the Group. The evolving requirements of the UK chemistry community, and in particular catalysis, for more challenging experiments, not only from the experimental environment conditions (more extreme gas concentrations, pressures and temperatures) but also requiring improved time resolution, lower loading samples, and the capability of mapping catalyst beds during the *operando* experiments will be greatly aided by the addition of SWIFT to the Spectroscopy beamline portfolio. An integrated design of the sample environment requirements and complementary techniques such as IR and mass spectrometers during the design phase, will optimise this beamline for *operando* studies. These characteristics will also be very attractive for the chemical industry, especially in the area of catalysis. As an example, an industry-funded beamline[10] at Spring-8 (TOYOTA Central R&D Labs., Inc.,) designed to study a wide variety of materials with applications in sustainable vehicle technologies, such as auto exhaust catalysts, secondary batteries and fuel cells, has very similar capabilities to SWIFT.

Finally, the proposed beamline will ease the demand on B18, that is currently oversubscribed by more than a factor of 3. Due to the unique characteristics of SWIFT, the combination of the new and existing beamlines will allow a more efficient use of the available beamtime on each spectrometer though reducing the need of changing between complex user configurations.

It is anticipated that the development of SWIFT will open up new opportunities for XAS in several fields of science that are currently not possible at Diamond, due to the combination of sub-second time resolution and a relatively small beam size.

4. Outline Specification

SWIFT will take advantage of the added capacity offered by Diamond-II. We are proposing to build the beamline on one of the new mid-straight sections that will become available within the new machine.

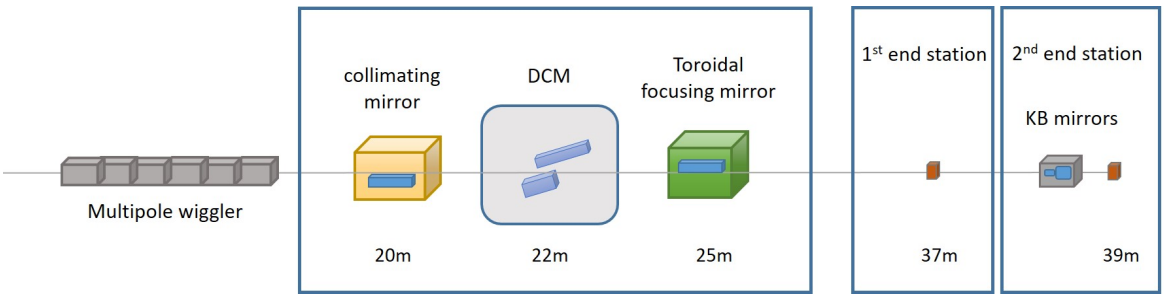

Figure 2. Proposed SWIFT layout, showing the position of the different optical elements and the two end-stations.

SWIFT is a XAS beamline operating in the energy range from 4keV to 34 keV covering all elements heavier than calcium, providing both, QuickEXAFS and step scanning capabilities. The beamline will house two

different end-stations. The first will operate with a beam size of around 100µm x 50µm FWHM (VxH), while a 18µm x 20µm FWHM (VxH) focal spot will be available in the second end station. This smaller beam size will be ideal for the investigation of heterogeneous samples on a 20µm scale and also for small sample volume high pressure studies.

The beamline will be based on a multipole wiggler, operating at 1.3T. The schematic optical layout is shown in Figure 2. The first optical element will be a vertical collimating mirror that will be used to achieve good energy resolution and to reduce the heat load impinging on the next optical element, a double crystal monochromator (DCM). The monochromator will be equipped with both Si(111) and Si(311) crystals to cover the entire energy range of the beamline. The monochromator will need to be optimized for both stepping and continuous scanning. This may require two independent devices to realize. After the DCM, a mirror focussing in the vertical and the horizontal planes will focus the beam at the first sample position (Figure 3 left). The flux at 12 keV using Si(111) at this first end-station will be of the order of $1x10^{13}$ ph/s. After this first end-station, a set of KB mirrors will be used to focus the beam size further into the second end-station (Figure 3 right). The flux at this end-station will be of the order of $3x10^{12}$ ph/s under the same conditions.

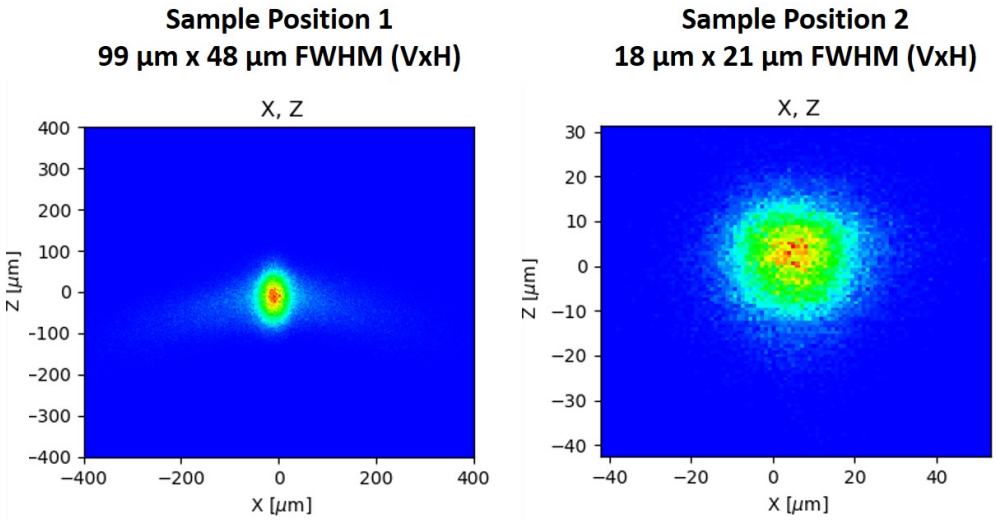

Figure 3. Shadow simulation of the focal spot obtained on the first end-station (left) and after refocussing the beam for the second end-station (right).

The beamline will be equipped with ion chambers to be used as transmission detectors and multielement germanium and silicon drift diode detectors will be used as fluorescence detectors. It is envisaged that the beamline will also be equipped with a portable X-ray emission spectrometer to be used in the second end-station to complement the XAS measurements.

The beamline will be optimized for the study of samples under *operando* conditions in a great variety of scientific disciplines. It is thus essential that it is equipped with a broad range of sample environment equipment: LN_2 and He cryostats for low temperature experiments, furnaces and plug flow reactors to study samples under high temperature or/and gas reactive mixtures, diamond anvil cells for studies of matter under high pressure, etc. This equipment will be shared with the rest of the beamlines in the Spectroscopy Group. In addition, we will supply the most common gases used in catalysis experiments to both end-stations as part of the infrastructure of the beamline. This will reduce the time needed to set up experiments, making the use of beamtime more efficient.

5. State of the art benchmark

X-ray Absorption Spectroscopy on fast time scales and/or with small focal spot sizes is performed at most synchrotrons. In this section the leading international beamlines have been chosen for comparison.

SWIFT will bring new capability for fast scanning spectroscopy at Diamond Light Source beyond what is currently offered at B18[11]. The beamline will facilitate sub-second scanning spectroscopy using a faster monochromator. The increased flux available compared to B18 will furthermore allow fluorescence mode QuickEXAFS which is currently limited by photon statistics.

Many other beamlines such as SuperXAS[9] at the SLS, ROCK[12] at Soleil, P64[13] at Petra III and the TOYOTA beamline[10], BL33XU, at Spring-8 use fast scanning monochromators to achieve sub-second time resolution, but in all cases the flux delivered to the sample is lower when compared with SWIFT. In the case of SuperXAS and ROCK, the flux is almost one order of magnitude smaller, as shown in Figure 4. Similar flux is delivered by BL33XU and P64, despite being based on insertion devices, as the undulator needs to be tapered to broaden the energy range needed for QuickEXAFS operation. SWIFT's higher flux and fast scanning capabilities will not only be competitive but will surpass the current beamlines optimized for the study of fast kinetics, especially fluorescence mode experiments limited by photon statistics.

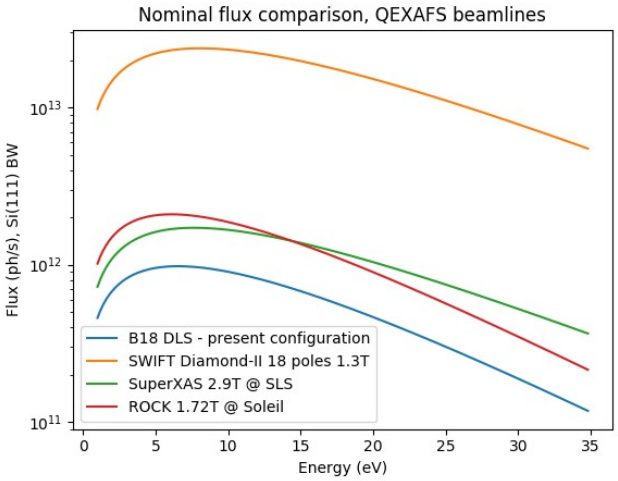

Figure 4. Flux comparison of some of the fast scanning beamlines in Europe.

SWIFT's second end-station, providing a focal spot of around 20x20 µm2, will be very complementary to both B18 and I18. Many of the existing XAS beamlines deliver focal spot sizes either similar to B18 (ROCK, SuperXAS and P64) or to I18 (BM23[14] at the ESRF and BL33XU when using the focusing capabilities). SWIFT will bring intermediate beam size capability that is currently not covered at Diamond.

6. Community engagement

Consultation with the user community will be critical for the success of a beamline such as the one proposed in this outline, as not only the optics and beam characteristics will be important, but also the sample environment equipment and complementary technique requirements will be essential to achieve state of the art *operando* performance. Due to the large size of the Diamond XAS user community, numbering well over 400 PIs in the last five years, we are proposing to form a working group with representative members of the many research disciplines covered, both from academia and industrial institutions. We will also ensure that large government initiatives such as the UK Catalysis Hub and the Faraday Institution are represented. We expect this group to collect the requirements of their colleagues and collaborators and communicate them to the working group.

In addition, an external champion for the project will be chosen. The champion will need to lead the full case that will presented to the Diamond management, SAC and DISCo.

7. References

1. Dann, E. K. *et al.* Combined spatially resolved operando spectroscopy: New insights into kinetic oscillations of

CO oxidation on Pd/Γ-Al2O3. *J. Catal.* **373**, 201–208 (2019).
2. Baumgartner, J. *et al.* Nucleation and growth of magnetite from solution. *Nat. Mater.* **12**, 310–314 (2013).
3. Wang, F., Cheng, S., Bao, Z. & Wang, J. Anisotropic overgrowth of metal heterostructures induced by a site-selective silica coating. *Angew. Chemie - Int. Ed.* **52**, 10344–10348 (2013).
4. Greenaway, A. G. *et al.* Detection of key transient Cu intermediates in SSZ-13 during NH3-SCR deNOx by modulation excitation IR spectroscopy. *Chem. Sci.* **11**, 447–455 (2020).
5. Genovese, C. *et al.* Operando spectroscopy study of the carbon dioxide electro-reduction by iron species on nitrogen-doped carbon. *Nat. Commun.* **9**, 1–12 (2018).
6. Yu, X. *et al.* High rate delithiation behaviour of LiFePO4 studied by quick X-ray absorption spectroscopy. *Chem. Commun.* **48**, 11537–11539 (2012).
7. Fabbri, E. *et al.* Dynamic surface self-reconstruction is the key of highly active perovskite nano-electrocatalysts for water splitting. *Nat. Mater.* **16**, 925–931 (2017).
8. Zhou, Y. N. *et al.* High-Rate Charging Induced Intermediate Phases and Structural Changes of Layer-Structured Cathode for Lithium-Ion Batteries. *Adv. Energy Mater.* **6**, 1–8 (2016).
9. Müller, O., Nachtegaal, M., Just, J., Lützenkirchen-Hecht, D. & Frahm, R. Quick-EXAFS setup at the SuperXAS beamline for in situ X-ray absorption spectroscopy with 10ms time resolution. *J. Synchrotron Radiat.* **23**, 260–266 (2016).
10. Nonaka, T. *et al.* Toyota beamline (BL33XU) at SPring-8. *AIP Conf. Proc.* **1741**, (2016).
11. Diaz-Moreno, S. *et al.* The Spectroscopy Village at Diamond Light Source. *J. Synchrotron Radiat.* **25**, 998–1009 (2018).
12. Briois, V. *et al.* ROCK: The new Quick-EXAFS beamline at SOLEIL. *J. Phys. Conf. Ser.* **712**, (2016).
13. Bornmann, B., Kläs, J., Müller, O., Lützenkirchen-Hecht, D. & Frahm, R. The quick EXAFS setup at beamline P64 at PETRA III for up to 200 spectra per second. *AIP Conf. Proc.* **2054**, (2019).
14. Mathon, O. *et al.* The time-resolved and extreme conditions XAS (Texas) facility at the European Synchrotron Radiation Facility: The general-purpose EXAFS bending-magnet beamline BM23. *J. Synchrotron Radiat.* **22**, 1548–1554 (2015).